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Metallated group IX and group X phosphinimine complexes.

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NOTE TO USERS

Metallated Group IX and Group X Phosphinimine Complexes

By
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Abstract

The focus of this research has been the preparation of late transition metal phosphinimine complexes. The thesis herein describes the synthesis of a series of monomeric Group IX phosphinimine complexes. [RhCOD(*o*-$C_6H_4PPh_2NR$)] (R= 2,6-$C_6H_3(CH_3)_2$ **44**, 2,6-$C_6H_3{}^iPr_2$ **45**, 3,5-$C_6H_3(CH_3)_2$ **46** and Ph **47**) were prepared *via* salt metathesis under mild conditions. The analogous complexes [Rh(*o*-$C_6H_4PPh_2NPh$)($Ph_2PCH_2CH_2PPh_2$)] **52** and [IrCOD(*o*-$C_6H_4PPh_2NPh$)] **53** were also readily prepared by similar methods. Reactivity studies were performed on these complexes. Unexpectedly, complexes **46**, **47**, **52** and **53** underwent oxidative addition of methylene chloride. However, when steric bulk was introduced on the 2,6-positions of the N-phenyl ring (compounds **44** and **45**), oxidative addition of CH_2Cl_2 was not observed.

The reaction of Group X transition metals with phosphinimine ligands was also explored. Attempts to coordinate [Li(*o*-$C_6H_4PPh_2NR$)]$_2$•Et_2O (R= $SiMe_3$ **61** and ^{t}Bu **62**) to Group X transition metals proved to be unsuccessful due to steric congestion. However, transmetallation did occur when less bulky phosphinimine ligands were used, such as, [Li(*o*-$C_6H_4PPh_2NR$)]$_2$•Et_2O (R= Ph **63** and 3,5-$C_6H_3(CH_3)_2$ **66**). The Group X phosphinimine complexes described herein, [Ni(*o*-$C_6H_4PPh_2NR)_2$] (R= Ph **67** and 3,5-$C_6H_3(CH_3)_2$ **68**) and [Pd(*o*-$C_6H_4PPh_2NPh)_2$] **69**, were *bis*-ligand type complexes.

"I have not failed. I have just found 10,000 ways that won't work."
— Thomas Alva Edison

If A equals success, then the formula is: A = X + Y + Z,
X is work. Y is play.
Z is keep your mouth shut.
— Albert Einstein

"Meeting challenges and enduring them, even though such experiences are often fraught with pain, is part of the great drive in human nature to expand beyond previously accepted limits."
— Michael Murphy

Acknowledgments

Graduate study is a test of endurance. The work presented in this thesis could not have been possible without the support of many people.

I wish to begin with expressing my sincere gratitude and appreciation to my supervisor, Dr. D. W. Stephan for his excellent supervision, continuous encouragement and valuable suggestion throughout the development of this work. I would also like to thanks Dr. S. J. Loeb and Dr. R. G. Maev for their role as my committee members.

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My heartfelt thanks to my family relentless support and encouragement throughout the years. Their confidences in me and continuing support have been vital to my ability in pursuing graduate studies.

Last but not least, I would like to thank a precious friend, Robert L. K. Yu for his endearing friendship, endless support and belief in me enabled me to successfully achieve a goal which at times seemed impossible to reach.

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Abbreviations

Å	Angstrom
Ar	aryl
atm	atmosphere
BIPE	bis((N-*p*-tolylimino)diphenylphosphoranyl) ethane
BIPM	bis(iminophosphoranyl) methane
Bn	benzyl (-$CH_2(C_6H_5)$)
br	broad
COD	cyclooctadiene
Co.	company
Cp	cyclopentadienyl anion (η^5-C_5H_5)
Cp*	pentamethylcyclopentadienyl anion (η^5-C_5Me_5)
Cy	cyclohexyl (C_6H_{12})
d	doublet
dd	doublet of doublets
DIPHOS	1,2-bis(diphenylphosphinoethane)
dt	doublet of triplets
°	Degree
°C	degrees of Celsius
δ	chemical shift
DME	dimethoxyethane
Et	ethyl (C_2H_5)
Et_2O	diethyl ether
EA	elemental analysis
eq	equivalent
F_c	calculated structure factor
F_o	observed structure factor
g	grams
η	hapto
h	hour
Hz	Hertz

^{i}Pr	iso-propyl (-CH(CH_3)$_2$)
J	coupling constant
^{2}J	two-bond coupling constant
^{3}J	three-bond coupling constant
MAO	methylaluminoxane
m	multiplet
Me	methyl (-CH_3)
min	minutes
mmol	millimols
NOESY	nuclear overhauser effect spectroscopy
NMR	Nuclear Magnetic Resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
o	ortho
p	para
Ph	phenyl (-C_6H_5)
ppm	parts per million
py	pyridine
pz	pyrazolate
R	agreement factor
R_w	weighted agreement factor
RT	room temperature
s	singlet
sept	septet
t	triplet
^{t}Bu	tertiary butyl (-C(CH_3))
THF	tetrahydrofuran
TMS	trimethylsilyl
Tol	tolyl ($C_6H_4CH_3$)
μ	bridging
α	alpha
β	beta
γ	gamma

Chapter One
Introduction

The continued development of well-defined transition metal complexes has had a huge impact on catalysis, especially single-site olefin polymerization catalysis.[1-3] Synthesis of new polymerization catalysts such as early metal metallocenes,[4,5] early metal non-metallocenes,[6] and recently, Schiff base-containing late metal systems[7-15] have generated intense interest because of the unique reactivity from each catalyst and the potential insight gained through understanding ligand-metal effects on the catalyst behavior. Within our own research group, attention has been focused primarily on catalysts that contain phosphinimide ligands. While investigating early transition metal complexes of phosphinimide ligands, we have shown that they can act as effective catalysts for ethylene polymerization upon activation with the appropriate co-catalyst.[16-22]

While early transition metal systems continue to be a fruitful area of study, recent interest has focused on late metal olefin polymerization catalysts, such as the work performed by Brookhart,[8,9,23-25] Gibson,[10-12,26] and most recently Grubbs.[14] These systems are very interesting, as they offer a unique approach to a variety of highly branched polyethylene. As part of our continuing efforts, we are exploring late metal complexes of phosphinimine and phosphinimide ligands. This introductory chapter briefly describes the historical development of the chemistry of Group IX and Group X transition metals. In addition, different types and properties of phosphinimine ligands, and previously reported phosphinimine metal complexes will be described.

1.1 Historical Development of Rhodium Chemistry

Rhodium is one of the least abundant elements in the earth's crust, and yet the chemistry of this metal is among the most diverse of all the transition metals and is being vigorously investigated at the present time.[27-32] Rhodium forms organometallic compounds in oxidation states ranging from +4 to -3, although by far the most common oxidation states are Rh(I) and Rh(III).

The first compound containing a rhodium-carbon bond was synthesized by Manchot and König in 1925 by treating [$RhCl_3$] with CO.[33] This complex was later formulated correctly by Hieber and Lagally[34] as the halogen bridged dimer [$Rh_2Cl_2(CO)_4$]. A decade later, Wilkinson and co-workers[35] reported the preparation and characterization of the rhodium cation, [$Rh(\eta\text{-}C_5H_5)_2$]$^+$. The first rhodium complex containing a rhodium-alkene bond [$\{RhCl(\eta^4\text{-}1,5\text{-}COD)\}_2$] was prepared by Chatt and Venanzi in 1956.[36] The same year, the first important class of rhodium carbonyl complex, which later developed into useful hydroformylation catalysts, [*trans*-$RhCl(CO)L_2$] (L=tertiary phosphine or arsine) was reported by Hieber and Heusinger.[37] Three years later, Fischer's group in Germany[38] and Wilkinson's group in England[39] simultaneously reported the discovery of the first rhodium compound containing a coordinated conjugated diene [$Rh(\eta\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)$]. Later, Cramer[40] discovered the first rhodium complex containing a monoalkene ligand [$\{RhCl(\eta\text{-}C_2H_4)_2\}_2$]. This discovery was quickly followed by the report of the first compounds containing a rhodium-carbon σ-bond [$RhBr(1\text{-naphthyl})_2L_2$] (L = tertiary phosphine) by Chatt and Underhill.[41] Perhaps the most important discovery which led to the explosion of interest in organorhodium chemistry came in 1965 when Wilkinson

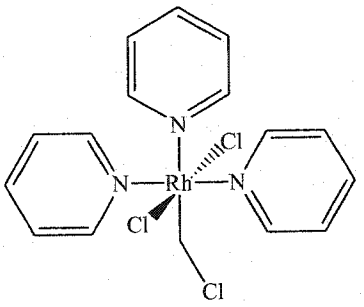
and his co-workers[42] reported that solutions of [$RhCl(PPh_3)_3$] would homogeneously catalyze the hydrogenation of alkenes and alkynes. Since then, there has been intense industrial and academic interest in the synthesis and chemistry of compounds containing rhodium-carbon and rhodium-hydrogen bonds.

1.2 Oxidative Addition of Chlorinated Solvents using Late Transition Metal Complexes

Oxidative addition is perhaps one of the most important factors governing catalytic reactions, since many catalytic cycles involve this process as a key step. Oxidative addition reactions of aliphatic compounds containing a C-X bond (X=Cl, Br or I) to low-valent transition metals are well documented.[43-52] There are many examples of oxidative addition reactions involving molecules of the type CH_3X (X=I or Br), and especially numerous are reports with more reactive species such as CH_2I_2, CH_2Br_2 and CH_2ICl.[53-55] Early reports of reactions with the solvents CH_2Cl_2 and $CHCl_3$ suggested that thermal[56] or photochemical[44,47,57] initiation was required. Recently though, several reactions involving oxidative addition of CH_2Cl_2 with transition metal complexes under mild conditions have been documented. In general, these reactions lead to products containing halomethyl (Cl-H_2C-M-Cl, or Cl-H_2C-M^+ X^-), methylene-bridged (X-M-CH_2-M-X) derivatives, or even metal carbene complexes.

The activation of dihalomethane by late metal transition metal complexes has been studied as a method of generating the metal-halomethane unit, M-CH_2X (X = halogen).[46,53,54,58-60] Throughout the years, examples of simple

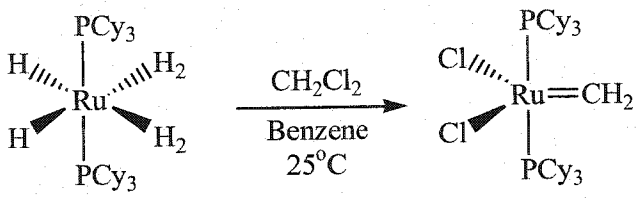
oxidative addition of CH_2Cl_2 to form chloromethyl complexes have been reported for electron-rich transition metal complexes containing mono-[61-63] or poly-dentate phosphine ligands,[64,65] bi- or tri-dentate nitrogen ligands,[66-68] sulfur macrocycles[69] and phosphorus-nitrogen hybrid ligands.[70-72] Heaton *et al.*,[60] for example, reported the synthesis of *mer*-[$Rh(py)_3(CH_2Cl)Cl_2$] **1** (Figure 1.1) from the reaction of [$Rh_2(C_8H_{14})_4(\mu\text{-}Cl)_2$] ($C_8H_{14}$ = cyclooctene) with pyridine in CH_2Cl_2.



1

Figure 1.1 *mer*-[$Rh(py)_3(CH_2Cl)Cl_2$]

Occasionally, double activation of the dihalomethane results in the formation of bridging methylene ($\mu\text{-}CH_2$) binuclear complexes. These reactions have been observed with the highly basic rhodium complexes [$Rh_2(dppe)_2(\mu\text{-}Cl)_2$],[73] [$Rh_2(PR_3)_4(\mu\text{-}Cl)_2$][74]($PR_3$=$PEt_3$ or PPh_2Me) and [$Rh_2(CN^tBu)_4(\mu\text{-}pz)_2$] (pz=pyrazolate).[75] The first type of double oxidative addition reaction of CH_2Cl_2 to a metal complex was reported in 1997 by Caulton *et al.*[76] [$RuH_2(H_2)_2L_2$][L=$P(C_6H_{11})_3$] underwent an unprecedented oxidative addition of both C-Cl bonds of CH_2Cl_2 to a single metal center, providing a convenient synthesis of the alkene metathesis catalyst [$RuCl_2(CH_2)\{P(C_6H_{11})_3\}_2$] **2** (Figure 1.2).



2

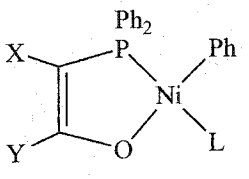
Figure 1.2 Synthesis of $[RuCl_2(CH_2)\{P(C_6H_{11})_3\}_2]$

1.3 Development of Late Transition Metal Catalysts

In recent years, there has been increasing interest in the development of late transition metal-based catalysts for the polymerization of α-olefins and functionalized olefins under ambient conditions.[77-81] The most notable catalysts thus far were reported by Brookhart and co-workers in 1995. They synthesized highly active cationic nickel (II) and palladium (II)-based catalysts of the type $[ArN=C(R)C(R)=NAr]M\text{-}CH_3^+$.[9,23,77,78,82] There are three key features of these α-diimine polymerization catalysts. First, the highly electrophilic cationic nickel and palladium metal centers result in rapid rates of olefin insertion. Second, the use of the sterically bulky α-diimine ligand favors insertion over chain transfer. Third, the use of noncoordinating counterions provides an accessible coordination site for the incoming olefin.[23]

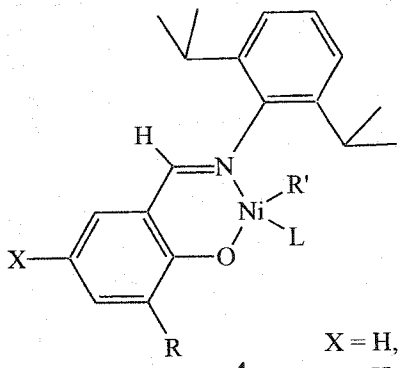
Late metal catalysts systems serve as a promising alternative to both traditional Ziegler-Natta[83,84] and metallocene catalysts.[85-88] Since early transition metal catalysts are highly oxophilic, they are incompatible with functionalized vinyl monomers.[89,90,91] Late transition metal catalysts are less oxophilic. Traditionally, however, they produced dimers or low-molecular weight oligomers due to chain termination *via* β-hydride elimination.[92-95]

However, Brookhart's late transition metal catalyst systems demonstrated the ability to produce high molecular weight polyethylene and poly α-olefins,[23] in addition to copolymerizing ethylene and functionalized olefins such as alkyl acrylates (when M = palladium).[77,78] There are only a limited number of late transition metal catalysts for the polymerization of high molecular weight polymers reported in the literature.[96-99] Most of them are based on either the neutral nickel (II) complexes[14,80,95,100-106] (Figure 1.3) of monoanionic bidentate ligands, or cationic nickel, palladium, iron, or cobalt complexes[8,9,23,77,78] (Figure 1.4) containing neutral multidentate ligands with bulky substituted nitrogen donor atoms.[10,24,107]



3

X = H, SO_3Na
Y = aryl, OR"
L = PR_3, subst. pyridine, CR_2PR_3



4

X = H, NO_2
R = H, aryl
R' = Me; L = CH_3CN
R' = Ph; L = PPh_3

Figure 1.3 Examples of neutral nickel (II) complexes

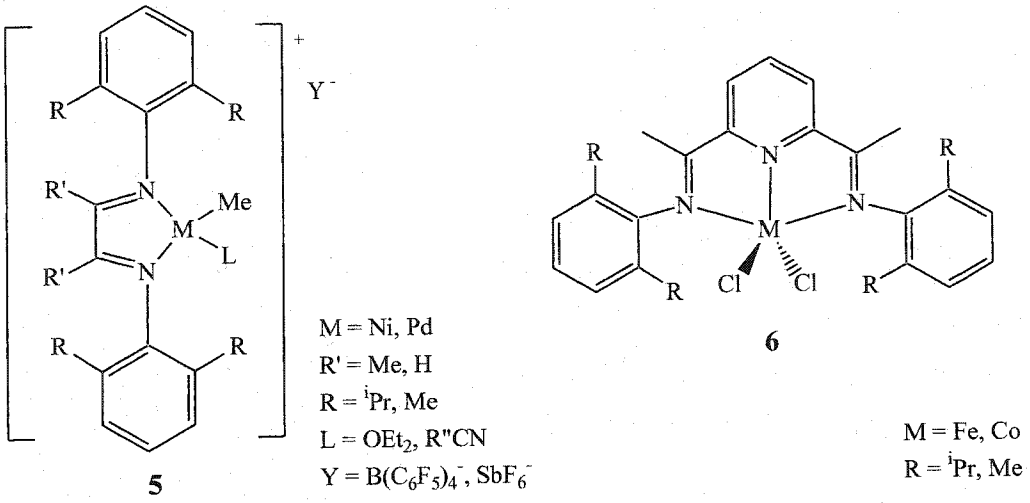


Figure 1.4 Examples of Ni, Pd, Fe and Co complexes

The recent discoveries of late transition metal catalysts are mostly based on the structural types shown in **4 – 6**, and these systems have spurred intense research for new late transition metal olefin polymerization catalysts using different types of ligand structures.

1.4 Synthesis and Types of Phosphinimine Ligands

Staüdinger first reported the preparation of phosphinimines in 1919 as the product of the redox reaction between tertiary phosphines (PR_3) with trimethylsilylazide ($TMSN_3$) to yield nitrogen gas and the corresponding triaryl- or trialkyl-phosphine silylimide (Figure 1.5).[108]

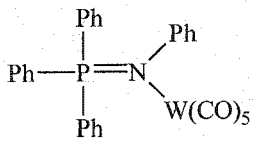
$$PR_3 + TMS\text{-}N_3 \longrightarrow R_3P{=}N\text{-}TMS + N_2$$

R = alkyl, aryl **7**

Figure 1.5 General equation of Staüdinger´s reaction

Monophosphazenes of the type $R_3P{=}NR'(R' \neq H)$ are commonly referred to as phosphinimines, phosphoranimines or imino phosphoranes. They are useful intermediates in the synthesis of natural products[109-111] and of nitrogen-containing organic compounds. The phosphinimine ligand can be represented as two resonance hybrids, $R_3P^+\text{-}N^-R$ and $R_3P{=}NR'$, and they are isoelectronic with phosphorus ylides. This kind of ligand framework is electronically very versatile, as it donates electron to the transition metal center resulting in strong MN bond character where M is a transition metal.

The nature of the highly polar P-N bond in the phosphinimine ligand makes it versatile in coordination and organometallic chemistry.[112-118] Variation of the substituents either on the nitrogen, or on the phosphorus atoms can both affect the basicity of the imine nitrogen, as well the steric and electronic properties of the phosphorus center.[119,120] The nitrogen atom of the phosphinimine acts as either a two-electron donor,[121-123] for example in $(CO)_5W(Ph_3PNPh)$ **8**, or as a four-electron donor, as in the bridging mode of $Mo_2(CO)_6(Ph_3PNH)_3$ **9** (Figure 1.6).[124]



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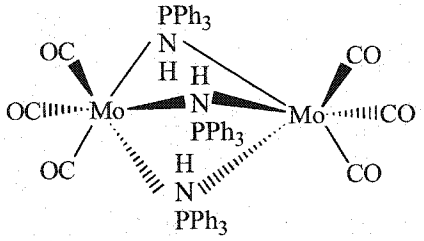

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Figure 1.6 Examples of the imine nitrogen of phosphinimine acting as a 2 or 4 e^- donor

As a result, the phosphinimine ligand offers a high degree of chemical flexibility that is useful when designing new organometallic compounds.

In general, there are several common approaches to synthesize phosphinimines. As was shown in Figure 1.5, the oxidation of a phosphine with the appropriate alkyl, aryl or silyl azide is the most commonly used method to generate phosphinimine compounds.[108] Another alternative is using N-lithiated phosphinimides (also known as lithium phosphonium azayldiides). They were initially prepared by Schmidbaur and Jonas[125] in 1967 by direct metallation of the corresponding phosphinimine[126,127] with a base such as methyl lithium in ether. In an extension of this chemistry, the corresponding N-substituted phosphinimine **11** can be obtained by reacting the N-lithiated phosphinimide **10** with a phosphorus electrophile (Figure 1.7).[125,128-130]

$$\underset{\textbf{10}}{R_3P{=}NLi} + R'_2PCl \longrightarrow \underset{\textbf{11}}{R_3P{=}N\text{-}PR'_2}$$

Figure 1.7 Reaction of a phosphorus electrophile with N-lithiated phosphinimde

Several research groups have demonstrated that introduction of a second phosphine moiety on the phosphinimine backbone to create a bidentate ligand is also possible (Figure 1.8).[131] This kind of ligand system is versatile, since it provides further possibility of developing new classes of ligand simply by changing the bridging species in the backbone. Cavell and co-workers have demonstrated that the controlled oxidation of *bis*(diphenylphosphino)methane (dppm) with trimethylsilyl azide produces the heterodifunctional phosphine-

phosphinimine **12** in good yield.[132-134] This reaction represents the first example of the selective oxidation of an alkane diphosphine with a nitrogen base.

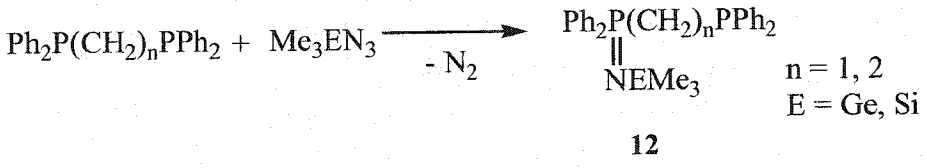

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Figure 1.8 Formation of phosphine-phosphinimine ligand system

This synthetic route can be applied to different bridged diphosphorus compounds and provides access to substituted phosphinimine-phosphine. Ligands of the type **12** are versatile, since they combine the ligating properties of the phosphinimines with those of the traditional tertiary phosphines.

Besides changing functional groups on phosphorus, functional groups attached to the nitrogen can also be easily modified.[135] Cavell and co-workers have demonstrated an alternative route to Staüdinger's reaction. They attached a nitro aromatic ring to the phosphinimine nitrogen through the reaction of the nitro fluoro aromatic with an iminosilylated phosphorus compound *via* the elimination of Me_3SiF.(Figure 1.9)[125] This reaction provides a safe route to synthesize nitro aromatic phosphinimine-phosphine ligands, while avoiding the preparation of explosive nitro aromatic azides which would be essential for the Staüdinger route.

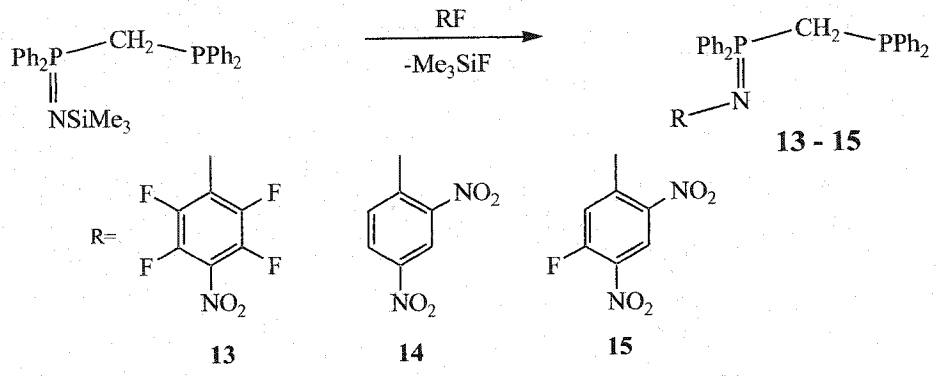


Figure 1.9 Alternative route to attach nitro-substituted arenes to the phosphinimine N atom

The bidentate form of phosphinimine ligands, such as *bis*(phosphinimine) methane [$CH_2(PR_2$=N-aryl$)_2$], [136-140] has also been thoroughly investigated.[136,137,141] *Bis*(methylenephosphoranyl)methane is analogous to 1,3-diketones. Elsevier *et al.*[142] proposed that it exists in two tautomeric forms although they could not establish such behaviour neither in solution nor in the solid state. (Figure 1.10).

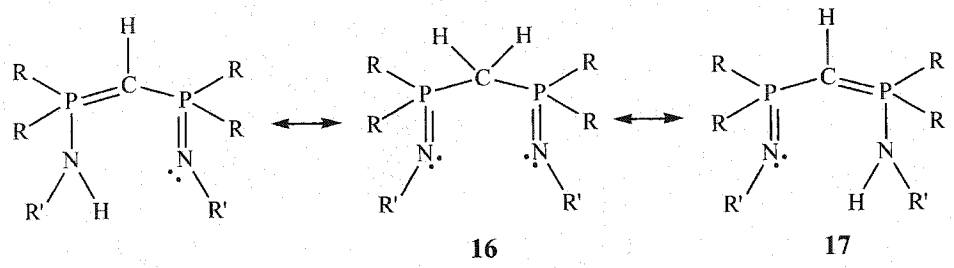


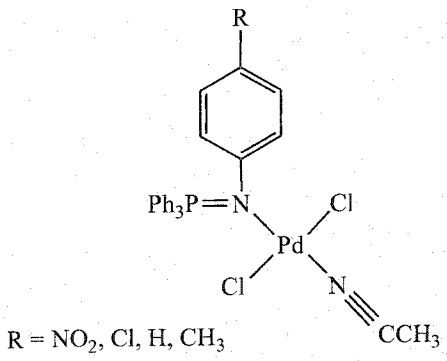
Figure 1.10 Tautomeric forms of *Bis*(phosphinimine)methane

Compound **16** is the typical representation of the ligand, whereas **17** is the tautomeric form, in which a proton migration has occurred from the central carbon atom to one of the nitrogen atoms. The two highly polarized P=N groups cause the methylene hydrogen atoms of tautomer **16** to be acidic,[143] therefore deprotonation of the methylene group readily occurs.

1.5 Metallated Phosphinimine Complexes

Since the first reports on the synthesis of phosphinimine ligands,[108] many investigations of the reactivity and coordination behavior of these compounds have been performed. There are few examples of a phosphinimine ligand acting as a four electron donor as in $Mo_2(CO)_6(HN{=}PPh_3)_3$ **9**, where each P=N ligand bridges *via* the nitrogen atom between the two Mo atoms. Since then, information on mono-phosphinimine complexes has been explored with metals such as: V,[144] Co,[145,146] Cu,[145] W,[147] Os,[148] Zn, Cd, Hg,[149] Al, Ge[128,150-152] and B.[153]

In 1975, Fukui and co-workers synthesized the first example of palladium(II) complexes with *p*-substituted phenyliminotriphenylphosphine **18** and N-trimethylsilyliminodiphenylmethylphosphine ligands **19** (Figure 1.11).[154]



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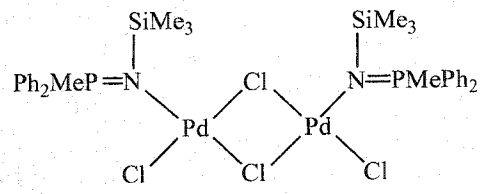

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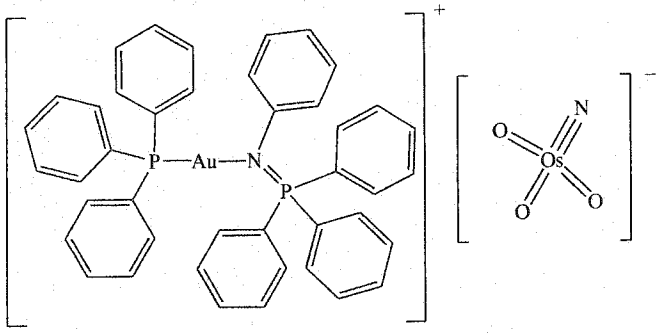
Figure 1.11 Pd(II) complexes with *p*-substituted phenyliminotriphenylphosphine and N-trimethylsilyliminodiphenylmethyl phosphine ligands

In efforts to try to obtain insight into the coordination properties and behaviour of the phosphinimine ligand, $R_3P{=}NR'$ toward different transition metals, in 1990, Elsevier synthesized the rhodium (I) phosphinimine complexes $[RhL_2Cl(RP{=}NR')]$ (R = Me_3, Et_3, Me_2Ph, Ph_3 and R′ = H, $SiMe_3$, ^tBu, Ph, *p*-tolyl). This was achieved by reacting $[RhLCl]_2$ (L = 2CO, COD) and the phosphinimine ligand in benzene or chloroform at room temperature.[155] In the same year, Cavell and co-workers synthesized the first structurally characterized example of a phosphinimine-phosphine palladium(II) complex, $RN{=}PPh_2(CH_2)_nEPh_2PdCl_2$ (R = $SiMe_3$, $GeMe_3$, H ; n = 1, 2 ; E = P, As).[134] In the following year, phosphinimine complexes of platinum(II) were reported.[156] Since then, late transition metal complexes containing phosphinimine groups have been extensively studied. In 1997, the first phosphinimine gold complex was isolated from the reaction of $[Au(PPh_3)(NOsO_3)]$ with Ph_3PNPh to yield the N-phosphinimine complex $[Au(PPh_3)(PhN{=}PPh_3)][NOsO_3]$ **20** (Figure 1.12).[157]

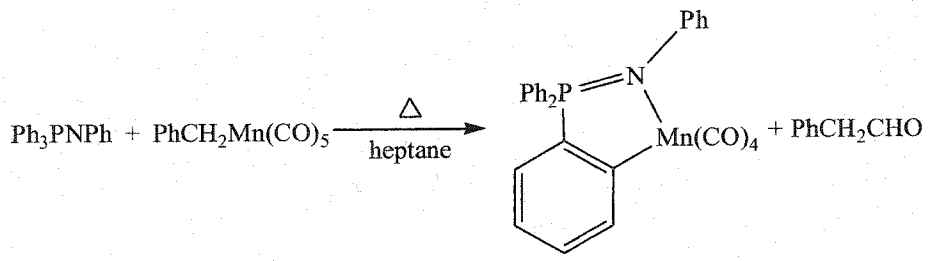


20

Figure 1.12 Structure of $[Au(PPh_3)(PhN{=}PPh_3)][NOsO_3]$

The combination of a reactive metal species and a polarized phosphinimine ligand has demonstrated some interesting reactivity. In 1999, Nicholson *et al.*

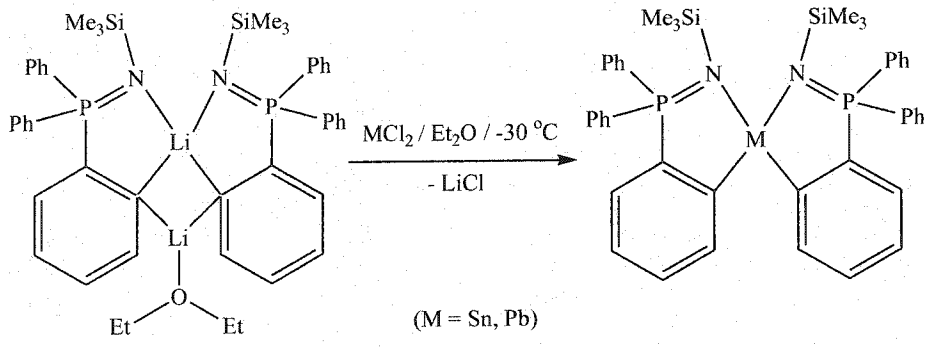
discovered the first example of cyclometallation of Ph_3PNPh with $PhCH_2Mn(CO)_5$ in refluxing heptane (Figure 1.13).[158]



21

Figure 1.13 *Ortho*manganation of Ph_3PNPh

Recently, Stalke *et al.* has examined the use of the deprotonated phosphinimine [*o*-$LiC_6H_4Ph_2P{=}NSiMe_3$][159] (formed from the lithiation of $Ph_3PNSiMe_3$ with MeLi) as a ligand for the stabilization of a series of diarylstannylene and plumbylene complexes (Figure 1.14).[160] They also successfully synthesized the corresponding organocopper complex, [$Cu(o$-$C_6H_4PPh_2NSiMe_3)]_2$, and the zinc complex, [$Zn(o$-$C_6H_4PPh_2NSiMe_3)]_2$, by reacting the same deprotonated phosphinimine with CuBr and $ZnCl_2$ respectively.[161]



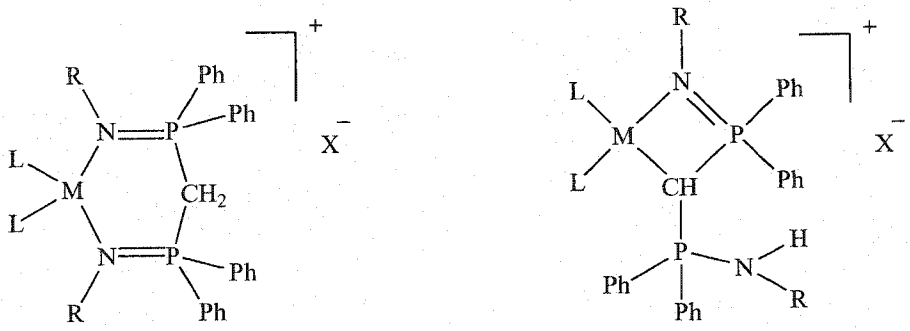
22 **23**

Figure 1.14 Reaction of [*o*-$LiC_6H_4Ph_2P{=}NSiMe_3$] with Sn(II) and Pb(II)

In these cases, a lithiated phosphinimine was chosen as a starting material because this complex provided the following requirements of an organometallic ligand capable of side arm donation. First, the deprotonated *ortho* phenyl carbon atom leads to a metal-carbon σ-bond in transmetallation reactions with metal halides. Secondly, the imine nitrogen atom donates its electron pair to the metal center for further stabilization.

Another class of phosphinimine compound, $[(Ph_2P{=}N\text{-}R)_2CH_2]$ (R=aryl, tolyl), which contain two phosphorus atoms were also fully investigated. The organometallic and coordination chemistry of this *bis*(iminophosphoranyl)methane (BIPM) ligand towards various transition metals such as Mo,[117] Rh,[133,142,162,163] Ir,[142,162-164] Pd,[134,165,166] and Pt[163,166,167] have been published. Previous reports have shown that reaction of the N-$SiMe_3$-substituted BIPM ligand with d^0 transition metals such as WX_6(X=Cl, F)[168] and OsO_4[169] resulted in the formation of N,N´-coordinated six membered metallacycles. The key feature in all these reactions involved the cleavage of the reactive Si-N bond, where heterocyclic compounds were being synthesized in all cases instead of forming phosphinimine complexes. Conversely, N-aryl substituted BIPM ligands have proven to be more suitable in reactions with late metals like Pt, Rh and Ir,[170] resulting in the formation of phosphinimine metal complexes. However, these reactions result in the formation of two isomers, **24** and **25**. The BIPM ligand acts as a σ-N, σ-N´ chelate in isomer **24**, and as a σ-N, σ-C chelated in isomer **25** (Figure 1.15). The alternative coordination mode in **25** is the result of the ability of one of the methylene protons to migrate to one

of the terminal N atoms.[171] Due to this proton migration, the formation of the four-membered metallacycles were unavoidable.



24 (M = Pd, Pt, Rh, Ir) **25**
(L = CO, COD, PR_3, Cl)
(R = *p*-tolyl, *p*-anisyl)
(X = Cl, Br, PF_6, BF_4, CF_3CO_2, ML_2Cl_2)

Figure 1.15 Different coordination modes of the reaction of BIPM with late metals

In 1996, Elsevier *et al*[172] successfully synthesized a modified version of the BIPM ligand by substituting the bridging CH_2 group with a $CHCH_3$ group. This modification introduced more steric hindrance around the central carbon atom, and hence favours stabilization of the σ-N, σ-N′ coordinated species. At the same time, the inductive electronic effect of the methyl group decreases the acidity of the methane proton. As a result, the reactions of $Pt_2Cl_4(PR_3)_2$ (PR_3 = PEt_3 or PMe_2Ph) with 1,1-*bis*((N-*p*-tolylimino)diphenylphosphoranyl) ethane (1,1-BIPE) **26** afforded the σ-N monodentate complex **27**. Conversion of **27** into the six membered platinacycle **28** took place after prolonged stirring in methylene chloride (Figure 1.16).

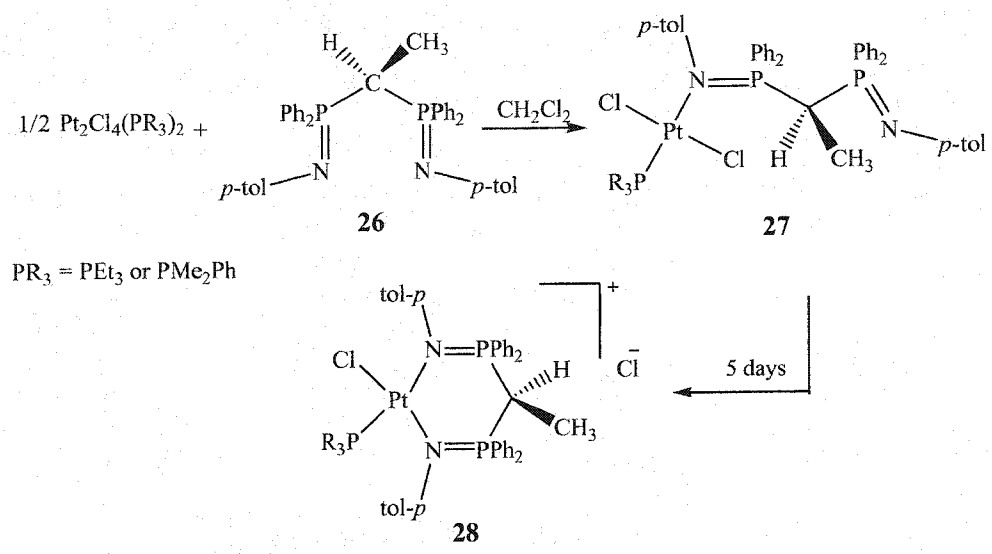


Figure 1.16 Reaction of $Pt_2Cl_4(PR_3)_2$ (PR_3=PEt_3 or PMe_2Ph) with 1,1-BIPE

Later, Stephan and Cavell simultaneously published their work on the mono- and di-lithiation of *bis*(diphenyl-*N*-trimethylsilylphosphinimino)methane.[139,143] Since the backbone CH_2 protons are moderately acidic, the ligand can be deprotonated by strong bases to generate the mono- and di-anionic species.[117] These compounds have proven to be convenient precursors for transmetallation reactions, forming various metal complexes (Figure 1.17).

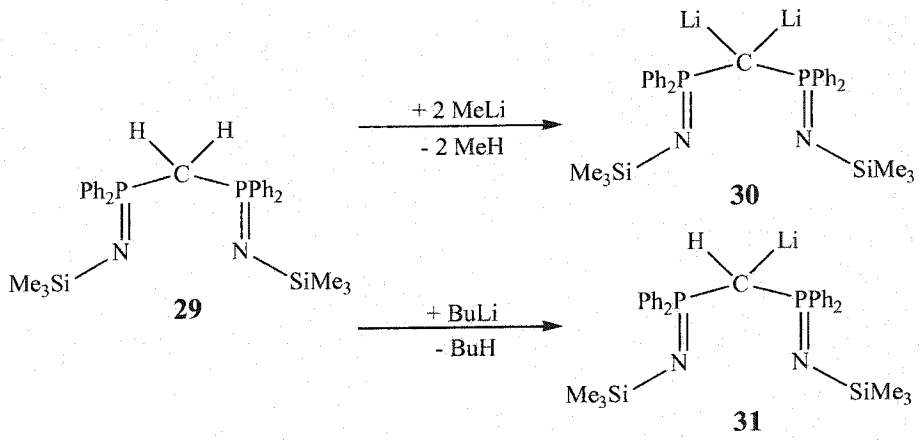
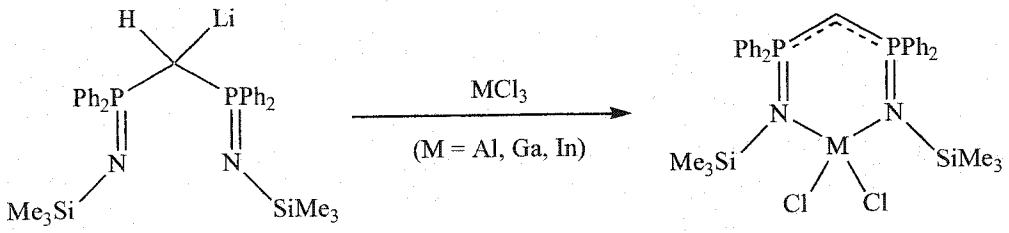


Figure 1.17 Mono or double deprotonation of $CH_2(Ph_2P{=}NSiMe_3)_2$

While not directly related to the present thesis, it is also noteworthy that besides reacting with late transition metal, these dilithiated *bis*(phosphinimine)methane are proven to form Ti, Zr[140,173] and bridging Cr carbene complexes.[174] Also, reaction of compound **31** with metals such as aluminum, gallium and indium halides readily yield four coordinate complexes of the form $[CH(PPh_2NSiMe_3)_2]MCl_2$ **32** (Figure 1.18).[175]



31 **32**

Figure 1.18 Reaction of $LiCH(Ph_2PNSiMe_3)_2$ with group 13 metals

Recently, Gambarotta *et al.* demonstrated the coordination of $VCl_3(THF)_3$ with the monolithium phosphinimine anion to afford the vanadium complex $[Me_3SiN{=}PPh_2CHPPh_2{=}NSiMe_3]VCl_2{\cdot}$toluene.[176]

1.6 Scope of Thesis

Over the past few years, our research group has been interested in phosphinimide ligands, and we have shown that titanium phosphinimide complexes can act as effective catalysts for ethylene polymerization upon activation. In recent years, the focus has been extended to the study of late transition metal phosphinimine complexes. Phosphinimine ligands offer a high degree of chemical flexibility through modification of the substituents on the

nitrogen or on the phosphorus atom. The combination of this anionic ligand to form neutral late transition metal complexes that possess a strong metal carbon σ-bond, may prove to be more stable than coordination bonds, thus imparting higher thermal stability. The original goal of this project was to prepare late transition metal complexes that possess a phosphinimine ligand in order to perform ethylene polymerization studies. Work in this thesis demonstrated substantial insight on the coordination studies of Group IX and Group X late transition metal complexes with phosphinimine ligands. Nonetheless, combining an electron rich Group IX metal with the polar phosphinimine ligand has shown some interesting chemistry. The thesis herein will focus on the synthesis of Group IX (Rh, Ir) and Group X (Ni, Pd, Pt) phosphinimine complexes, in addition to a preliminary investigation of their reactivities.

Chapter Two

Synthesis of Group IX Phosphinimine Complexes

2.1 Introduction

Throughout the years, our laboratory has endeavored to discover new families of highly active catalysts for olefin polymerization when activated with activators. Based on the similarities of the electronic and steric properties between cyclopentadienide and phosphinimide ligands, we have focused our attention on the development of early transition metal complexes containing phosphinimide ligands. For example, titanium phosphinimide complexes are very active catalysts for olefin polymerization when activated with MAO, $B(C_6F_5)_3$, or $[Ph_3C][B(C_6F_5)_4]$.[16,17] In recent years, our group has broadened our studies to include late transition metal olefin polymerization catalysts, since related systems supported by α-diimine ligands have demonstrated the potential to effect olefin polymerization catalysts upon activation. In order to explore this area, our research has been centered around studies of Group IX and Group X late metal complexes containing phosphinimine ligands. This chapter outlines the synthesis of Group IX phosphinimine complexes, and subsequently, the intriguing chemistry of the reaction between the solvent methylene chloride and the late metal compounds.

2.2 Experimental

General Data: All preparations were performed under an atmosphere of dry, anaerobic N_2 gas employing either Schlenk line techniques or a Mbraun inert atmosphere glove box. All glassware were oven-dried overnight prior to use.

THF, diethyl ether, toluene, and pentane were distilled from sodium benzophenone ketyl under nitrogen. CH_2Cl_2 was dried over CaH_2 and distilled under nitrogen. C_6D_6, CD_2Cl_2 and THF-d_8 were degassed by the freeze-thaw method at least three times prior to use. Ph_3PNPh and DIPHOS were used as received from Aldrich Chemical Co. ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^7Li\{^1H\}$ and ^2D NMR spectra were recorded on Bruker Avance 300 MHz or 500 MHz spectrometers. Trace amounts of protonated solvents were used as references and ^1H, $^{31}P\{^1H\}$ and $^7Li\{^1H\}$ chemical shifts are reported relative to $SiMe_4$, 85% H_3PO_4 and LiCl respectively. Combustion analyses were performed by the Center for Catalysis and Materials Research (CCMR), Windsor, Ontario, Canada. X-ray structure solution and refinement calculations were performed by Dr. P. Wei.

General Information on X-Ray Data Collection and Reduction

All X-ray data collection, data reduction, solution structure and refinements obtained in this thesis were performed using the same method; thus only one general description is given. Deviation will be noted in appropriate sections of the thesis.

X-ray quality crystals were manipulated and mounted in 0.5 mm capillaries in a glove box, thus a dry, O_2-free environment for each crystal was maintained. Diffraction experiments were performed on a Siemens Smart systems CCD diffractometer employing graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) and collecting a hemisphere of data with 30-second exposure times. Data were further processed using the SHELX crystallographic

software operating on a Pentium computer. An empirical absorption correction was applied to the data using SADABS. The reflections with $F_o^2 > 3\sigma F_o^2$ were used in the refinements.

General Information of Structure Solution and Refinement

Non-hydrogen atomic scattering factors were taken from literature tabulations.[177] Atom positions were determined either by SHELXTL-93 direct methods or a Patterson routine with successive difference Fourier map calculations. Refinements were carried out by full-matrix least-squares technique on *F* minimizing the function $\omega(|F_o| - |F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of refinements, all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atom positions were calculated to ride on the carbon atoms to which they were bound assuming a C-H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 120% of the temperature factors of the carbon atoms to which they were bound. All hydrogen atom contributions were calculated but not refined. After final cycles of refinement, no chemically significant residual electron density was observed.

Synthesis of arylazides: N_3-2,6-$C_6H_3(CH_3)_2$ *33*, N_3-2,6-$C_6H_3{}^iPr_2$ *34* and N_3-*3*,5-$C_6H_3(CH_3)_2$ *35*[178]

Compounds ***33-35*** were prepared by similar methods, thus only one representative procedure is described. A mixture of 2,6-dimethylphenylaniline

(12.0g, 99 mmol) and $NaNO_2$ (7.5g, 109 mmol) were added to a cooled (-30°C) acidic (40 mL conc. HCl and 40 mL distilled H_2O) solution of $NaBF_4$ (21.7g, 198 mmol). After several minutes of stirring, a yellow precipitate gradually formed, and the mixture was stirred at -30°C for 30 minutes. The slightly air-sensitive tetrafluoroborate salt was filtered quickly in air and washed with cold H_2O. The yellow salt was added portion wise to a cooled (0 °C) aqueous solution (100 mL) of NaN_3 (19.3g, 297 mmol). After vigorous gas evolution, the orange mixture was stirred overnight at room temperature. The product was extracted from the aqueous layer with diethyl ether (3 x 10 mL) and dried over anhydrous $MgSO_4$. The solution was filtered, and the solvent removed to give a red oil (7.5g, 61mmol). The oil was used without purification due to the risk of explosion. ***33***: ^1H NMR (500 MHz, $CDCl_3$) δ: 6.96 (m, 2H, C_6H_3), 6.67 (m, 1H, C_6H_3), 2.21 (s, 6H, CH_3). ***34***: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.07-7.21 (m, 3H, C_6H_3), 3.38 (m, 2H, ^{i}Pr), 1.28 (m, 12H, ^{i}Pr). ***35***: ^1H NMR (500 MHz, $CDCl_3$) δ: 7.08 (s, 2H, C_6H_3), 6.42 (m, 1H, C_6H_3), 2.38 (s, 6H, CH_3). $^{13}C\{^1H\}$NMR agreed with literature data.

Synthesis of Ph_3P=N(2,6-$C_6H_3(CH_3)_2$) *36*, Ph_3P=N(2,6-$C_6H_3{}^iPr_2$) *37*, Ph_3P=N(3,5-$C_6H_3(CH_3)_2$) *38*

Compounds ***36-38*** were prepared by similar methods, thus only one representative procedure is described. A solution of 2,6-dimethylphenyl azide (1.2g, 9.9mmol) in CH_2Cl_2 (2 mL) was added dropwise at RT to a solution of PPh_3 (1.3g, 4.9mmol) in the same solvent (5 mL). The homogeneous solution was stirred overnight and was then concentrated to approximately 2 mL *in*

vacuo. Pentane (5 mL) was added, and a pale yellow solid precipitated out of solution. The product was filtered, washed with cold pentane (3 x 5 mL) and dried *in vacuo*. **36**: Yield: 1.12g (64%). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.70-7.66 (m, 6H, $^{3}J_{P-H}$=12Hz, PPh_3), 7.14 (m, 2H, $C_6H_3(CH_3)_2$), 7.05-7.02 (m, 3H, PPh_3), 7.00-6.96 (m, 6H, PPh_3), 6.89 (d, 1H, $^{1}J_{H-H}$=7Hz, $C_6H_3(CH_3)_2$), 2.24 (s, 6H, CH_3) $^{13}C\{^{1}H\}$NMR (75.5MHz, C_6D_6) δ: 147.9 (s, $C_6H_3(CH_3)_2$), 135.1 (s, $C_6H_3(CH_3)_2$), 133.8 (s, PPh_3), 132.5 (d, $^{2}J_{P-C}$=8Hz, PPh_3), 131.2 (s, PPh_3), 128.5 (s, PPh_3), 119.1 (s, $C_6H_3(CH_3)_2$), 118.5 (s, $C_6H_3(CH_3)_2$), 21.8 (s, CH_3). $^{31}P\{^{1}H\}$NMR (202.5 MHz, C_6D_6) δ: -9.8.

37: Yield: 1.34g (80%). ^{1}H NMR (300 MHz, C_6D_6) δ: 7.69-7.62 (m, 6H, PPh_3), 7.23 (d, 2H, $^{1}J_{H-H}$=8Hz, $C_6H_3{}^{i}Pr_2$), 6.96-7.11 (m, 10H), 3.68-3.53 (sept, 2H, $^{1}J_{H-H}$=7Hz, ^{i}Pr), 1.09 (d, 12H, $^{1}J_{H-H}$=7Hz, ^{i}Pr) $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6) δ: 142.7 (d, $^{2}J_{P-C}$=7Hz, $C_6H_3{}^{i}Pr_2$), 134.4 (s, ^{i}Pr), 133.0 (s, PPh_3), 132.3 (d, $^{2}J_{P-C}$=9Hz, PPh_3), 130.9 (s, PPh_3), 128.3 (d, $^{3}J_{P-C}$=12Hz, PPh_3), 123.1 (s, $C_6H_3{}^{i}Pr_2$), 119.9 (s, $C_6H_3{}^{i}Pr_2$), 28.9 (s, ^{i}Pr), 23.8 (s, ^{i}Pr). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, C_6D_6) δ: - 8.9. Anal. Calc'd for $C_{30}H_{32}PN$: C, 82.35; H, 7.37; N, 3.20. Found: C, 82.46; H, 7.42; N, 3.19.

38: Yield: 1.02g (70%). ^{1}H NMR (500 MHz, C_6D_6) δ: 7.88-7.81 (m, 6H, PPh_3), 7.07-6.96 (m, 9H, PPh_3), 6.93 (s, 2H, $C_6H_3(CH_3)_2$), 6.48 (s, 1H, $C_6H_3(CH_3)_2$), 2.19 (s, 6H, CH_3). $^{13}C\{^{1}H\}$NMR (75.5MHz, C_6D_6) δ: 152.0 (s, PPh_3), 138.0 (s, $C_6H_3(CH_3)_2$), 133.1 (d, $^{2}J_{P-C}$=9Hz, PPh_3), 132.1 (s, $C_6H_3(CH_3)_2$), 131.5 (d, $^{4}J_{P-C}$=2Hz, PPh_3), 128.7 (d, $^{3}J_{P-C}$=12Hz, PPh_3), 122.2 (d, $^{3}J_{P-C}$=18Hz, $C_6H_3(CH_3)_2$), 120.2 (s, $C_6H_3(CH_3)_2$), 21.3 (s, CH_3). $^{31}P\{^{1}H\}$NMR (202.5 MHz, C_6D_6) δ: -1.5.

Ortho-lithiation of $Ph_3P{=}N(2,6\text{-}C_6H_3(CH_3)_2)$ with LiMe 40

$Ph_3P{=}N(2,6\text{-}C_6H_3(CH_3)_2)$ (0.2g, 0.52mmol) was dissolved in Et_2O (5 mL), and LiMe (0.45mL, 0.63mmol) was added dropwise at RT. The solution turned yellow immediately, and gradually changed color to light orange. The mixture was stirred overnight, after which time the solvent was removed *in vacuo.* Yield: 0.18g (85%). ^1H NMR(500 MHz, C_6D_6) δ: 8.51 (br, 2H, PC_6H_4), 7.54-7.51 (m, 8H, PPh_2), 7.28 (br, 2H, $C_6H_3(CH_3)_2$), 7.04-7.00 (m, 8H, PPh_2), 6.96-6.93 (m, 12H), 6.81-6.79 (m, 2H, PC_6H_4), 3.12-3.08 (m, 4H, CH_2), 1.96 (s, 12H, $C_6H_3(CH_3)_2$), 0.90-0.85 (m, 6H, $CH_2\mathbf{C}H_3$). $^{13}C\{^1H\}$NMR (75.5MHz, C_6D_6) δ: 147.8 (s, $C_6H_3(CH_3)_2$), 141.9 (s, $C_6H_3(CH_3)_2$), 141.2 (s, PC_6H_4), 134.5 (d, $^1J_{P\text{-}C}$=7 Hz, PPh_2), 133.2 (s, PC_6H_4), 132.7 (d, $^2J_{P\text{-}C}$=8 Hz, PPh_2), 131.6 (s), 130.2 (s), 128.7 (s), 123.4 (s), 120.5 (s, PC_6H_4), 65.1 (s, CH_2), 20.7 (s, $C_6H_3(CH_3)_2$), 14.5 (s, $CH_2\mathbf{C}H_3$). $^7Li\{^1H\}$NMR (194.4 MHz, C_6D_6) δ: 3.38. $^{31}P\{^1H\}$NMR (202.5 MHz, C_6D_6) δ: 15.2.

Ortho-lithiation of $Ph_3P{=}N(2,6\text{-}C_6H_3{}^iPr_2)$ with LiMe 41

$Ph_3P{=}N(2,6\text{-}C_6H_3{}^iPr_2)$ (0.12 g, 0.27 mmol) was dissolved in Et_2O (5mL) , and LiMe(1.4M in Et_2O) (0.24 mL, 0.33 mmol) was added dropwise at RT. The homogeneous yellow solution was stirred for 12 days during which time the solution became light orange in color. The solvent was removed *in vacuo,* and the residue was washed with benzene to afford a yellow solid. Yield: 0.14 g (52%). ^1H NMR (500 MHz, C_6D_6) δ: 8.61 (d, 2H, $^3J_{H\text{-}H}$=7Hz, PC_6H_4), 7.54-7.48 (m, 8H, PPh_2), 7.25-7.23 (m, 4H, $C_6H_3{}^iPr_2$), 7.10-6.89 (m, 20H), 3.71-3.58 (sept, 4H, $^3J_{H\text{-}H}$=7Hz, ^{i}Pr), 3.27-3.21 (m, 4H, CH_2), 1.22 (br, 12H, ^{i}Pr), 1.10-1.06 (m,

6H, CH_2CH_3), 0.57 (br, 12H, ^iPr). $^{13}C\{^1H\}$NMR (75.5MHz, C_6D_6) δ: 145.2 (d, $^1J_{P-C}$=7Hz, PC_6H_4), 144.6 (s, $C_6H_3{}^iPr_2$), 142.7 (d, $^1J_{P-C}$=7Hz, PPh_2), 134.4 (s), 133.1 (d, $^2J_{P-C}$=8Hz, PC_6H_4), 132.4 (d, $^2J_{P-C}$=9Hz, PPh_2), 130.9 (s, PPh_2), 130.6 (s), 124.3 (s), 123.5 (s, $C_6H_3{}^iPr_2$), 122.3 (s), 119.9 (s), 65.7 (s, CH_2), 28.9 (s, $C_6H_3{}^iPr_2$), 23.8 (s, ^iPr), 15.3 (s, $CH_2\mathbf{C}H_3$). $^7Li\{^1H\}$NMR (194.4 MHz, C_6D_6) δ: 6.73. $^{31}P\{^1H\}$NMR (202.5 MHz, C_6D_6) δ: 18.4.

Ortho-lithiation of Ph_3P=N(3,5-$C_6H_3(CH_3)_2$) with Li^{n}Bu 42

Ph_3P=N(3,5-$C_6H_3(CH_3)_2$) (0.2g, 0.52mmol) was dissolved in Et_2O (5mL), and ^{n}BuLi (2.5M in hexane), (0.25mL, 0.63mmol) was added dropwise at RT. The solution turned dark red immediately. The mixture was stirred overnight, after which time the solvent was removed *in vacuo.* Yield: 0.13g (63%). ^1H NMR (300 MHz, C_6D_6) δ: 8.28 (m, 2H, PC_6H_4), 7.85-7.75 (m, 8H, PPh_2), 7.32-7.26 (m, 2H, PC_6H_4), 7.18 (m, 2H, PC_6H_4), 7.08-6.93 (m, 16H), 6.36-6.35 (m, 4H, $C_6H_3(CH_3)_2$), 2.10-1.97 (m, 12H, $C_6H_3(CH_3)_2$), 2.82 (m, 4H, CH_2), 0.49 (m, 6H, CH_2CH_3). $^{13}C\{^1H\}$NMR (75.5MHz, C_6D_6) δ

Ortho-lithiation of Ph_3P=NPh with LiPh 43[179]

Ph_3P=NPh (0.15g, 0.42mmol) was dissolved in Et_2O (5 mL), and LiPh (0.3mL, 0.55mmol) was added dropwise at RT. The imide dissolved slowly and a yellow precipitate formed gradually. The mixture was allowed to stir overnight. The precipitate was then filtered, washed with diethyl ether and dried *in vacuo*. Yield: 0.16g (47%). ^{1}H NMR (500 MHz, C_6D_6) δ: 8.28 (d, 2H, $^3J_{H-H}$ = 7Hz, PC_6H_4), 7.89 (m, 8H, PPh_2), 7.28 (m, 4H, NPh), 7.09-6.95 (m, 14H), 6.89-6.94 (m, 8H, PPh_2), 6.61 (m, 2H, PC_6H_4), 3.35-3.31 (m, 4H, CH_2), 1.17-1.14 (m, 6H, CH_2CH_3). $^{13}C\{^1H\}$NMR (75.5MHz, C_6D_6) δ: 151.7 (s, NPh), 142.1 (s, PC_6H_4), 133.4 (d, $^2J_{P-C}$ = 9Hz, PPh_2), 132.5 (s, PPh_2), 131.5 (s, PC_6H_4), 130.8 (s), 129.5-129.8 (m, NPh), 128.8-128.5 (m), 124.5-123.9 (m), 123.3 (s, PPh_2), 117.9 (s, PC_6H_4, 65.6 (s, CH_2), 14.9 (s, CH_2CH_3). $^7Li\{^1H\}$NMR (194.4 MHz, C_6D_6) δ: 4.2. $^{31}P\{^1H\}$NMR (202.5 MHz, C_6D_6) δ: 18.1.

Synthesis of [RhCOD(*o*-$C_6H_4PPh_2N(2,6-C_6H_3(CH_3)_2)$)] 44, [RhCOD(*o*-$C_6H_4PPh_2N(2,6-C_6H_3{}^iPr_2)$)] 45, [RhCOD(*o*-$C_6H_4PPh_2N(3,5-C_6H_3(CH_3)_2)$)] 46, [RhCOD(*o*-$C_6H_4PPh_2NPh$)] 47

Compounds **44-47** were prepared by similar methods, thus only one representative procedure is described. A mixture of [Li(*o*-$C_6H_4PPh_2N(2,6-C_6H_3(CH_3)_2)$)]$_2$•$Et_2O$ (0.26g, 0.31mmol) and [RhCl(COD)]$_2$ (0.22g, 0.44mmol) was dissolved in THF (5 mL) at RT. The homogeneous reddish solution was stirred overnight, after which time the solvent was removed *in vacuo*. The residue was washed with pentane and recrystallized from THF/Et_2O or THF/C_6D_6. **44**: Yield: 0.08g (43%). ^{1}H NMR (500MHz, C_6D_6) δ: 7.60-7.56 (m,

5H, PPh_2), 7.25 (d, 1H, $^2J_{Rh-H}$=7 Hz, PC_6H_4), 6.96-6.82 (m, 11H), 4.18-4.17 (m, 2H, COD), 3.95-3.94 (m, 2H, COD), 2.56-2.54 (m, 2H, COD), 2.38-2.36 (m, 2H, COD), 2.12 (s, 6H, $C_6H_3(CH_3)_2$), 2.07-2.04 (m, 2H, COD), 1.94-1.91 (m, 2H, COD). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ: 173.5 (d, $^1J_{Rh-C}$=41Hz, PC_6H_4), 145.4 (s, $C_6H_3(CH_3)_2$), 136.5 (s, $C_6H_3(CH_3)_2$), 135.5 (s, PC_6H_4), 132.8 (d, $^2J_{P-C}$=9Hz, PPh_2), 131.1 (s), 130.9 (s, PPh_2), 129.9 (s, PC_6H_4), 129.8 (s, PC_6H_4), 129.6 (s, PC_6H_4), 128.2 (s) 123.9 (m), 94.4 (d, $^1H_{Rh-C}$=7Hz, COD), 68.8 (d, $^1J_{Rh-C}$=15Hz, COD), 32.3 (s, COD), 30.0 (s, COD), 20.9 (s, $C_6H_3(CH_3)_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6) δ: 43.3 (d, $^2J_{Rh-P}$=11Hz). Anal. Calc'd for $C_{34}H_{35}PNRh$: C, 69.04; H, 5.96; N, 2.37. Found: C, 68.61; H, 5.70; N, 2.28.

45: Yield: 0.08g (43%). ^1H NMR (500MHz, C_6D_6) δ: 7.78-7.74 (m, 4H, $^3J_{P-H}$=9Hz, PPh_2), 7.51 (d, 1H, $^3J_{Rh-H}$=8Hz, PC_6H_4), 7.19 (s, 1H, PC_6H_4), 7.02-6.99 (m, 4H, PPh_2), 6.97-6.93 (m, 2H, $C_6H_3{}^iPr_2$), 6.92-6.86 (m, 5H), 4.24-4.18 (m, 4H, $^1J_{Rh-H}$=26Hz, COD), 2.54-2.41 (m, 4H, COD), 2.01-1.96 (m, 4H, COD), 1.52 (d, 6H, $^1J_{H-H}$=7Hz, ^{i}Pr), 0.40 (d, 6H, $^1J_{H-H}$=7Hz, ^{i}Pr). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ: 173.6 (d, $^1J_{Rh-C}$=40Hz, PC_6H_4), 146.5 (d, $^1J_{P-C}$=6Hz, PPh_2), 143.0 (d, $^1J_{P-C}$=5Hz, PC_6H_4), 140.3 (s, $C_6H_3{}^iPr_2$), 135.5 (d, $^2J_{Rh-C}$=18Hz, PC_6H_4), 132.7 (d, $^2J_{P-C}$=8Hz, PC_6H_5), 131.4 (s, ^{i}Pr), 131.3 (s, $C_6H_3{}^iPr_2$), 130.3 (s, ^{i}Pr), 129.6 (s, PC_6H_4), 129.4 (s), 124.1 (s), 123.8 (d, $^3J_{P-C}$=3Hz, PPh_2), 123.3 (s), 123.1 (s), 92.8 (d, $^1J_{Rh-C}$=7Hz, COD), 69.4 (d, $^1J_{Rh-C}$=15Hz, COD), 32.2 (s, COD), 30.0 (s, COD), 28.5 (s, ^{i}Pr), 25.3 (s, ^{i}Pr), 23.9 (s, ^{i}Pr). $^{31}P\{^1H\}$ NMR (202.5MHz, C_6D_6) δ: 39.9. Anal. Calc'd for $C_{38}H_{43}PNRh$: C, 70.47; H, 6.69; N, 2.16. Found: C, 69.59; H, 6.89; N, 2.25.

46: Yield: 0.09g (60%). ^{1}H NMR (500MHz, C_6D_6) δ: 7.69-7.65 (m, 4H, PPh_2), 7.55 (d, 1H, $^{3}J_{H-H}$=7Hz, PC_6H_4), 7.23 (d, 1H, $^{3}J_{H-H}$=7Hz, PC_6H_4), 7.04 (m, 1H, $^{3}J_{H-H}$=7Hz, PC_6H_4), 7.00-6.98 (m, 2H, PPh_2), 6.93-6.88 (m, 5H), 6.65 (s, 2H, $C_6H_3(CH_3)_2$), 6.47 (s, 1H, $C_6H_3(CH_3)_2$), 4.47 (m, 2H, COD), 4.15 (m, 2H, COD), 2.57 (m, 2H, COD), 2.43 (m, 2H, COD), 2.07 (m, 2H, COD), 2.01 (m, 2H, COD), 1.97 (s, 6H, $C_6H_3(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, C_6D_6) δ: 174.1 (d, $^{1}J_{Rh-C}$=40Hz, PC_6H_4), 147.9 (s, PC_6H_4), 141.9 (s, $C_6H_3(CH_3)_2$), 137.5 (s, PPh_2), 135.4 (d, $^{2}J_{P-C}$=18Hz, PC_6H_4), 133.5 (d, $^{1}J_{P-C}$=9Hz, PPh_2), 131.7 (s, PC_6H_4), 130.3 (s, $C_6H_3(CH_3)_2$), 130.0 (s, PC_6H_4), 128.6 (s), 128.4 (s), 127.4 (d, $^{3}J_{Rh-C}$=7Hz, $C_6H_3(CH_3)_2$), 125.1 (s, $C_6H_3(CH_3)_2$), 123.4 (s), 93.8 (d, $^{1}J_{Rh-C}$=7Hz, COD), 69.1 (d, $^{1}J_{Rh-C}$=15Hz, COD), 32.6 (s, COD), 30.1 (s, COD), 21.4 (s, $C_6H_3(CH_3)_2$). $^{31}P\{^{1}H\}$ NMR (202.5MHz, C_6D_6) δ: 47.6. Anal. Calc'd for $C_{34}H_{35}PNRh$: C, 69.04; H, 5.96; N, 2.37. Found: C, 69.00; H, 6.51; N, 2.24.

47: Yield: 0.24g (60%). ^{1}H NMR (300MHz, C_6D_6) δ: 7.67-7.61 (m, 4H, PPh_2), 7.55-7.53 (m, 1H, $^{3}J_{P-H}$=8Hz, PC_6H_4), 7.24-7.18 (m, 1H, $^{3}J_{H-H}$=7Hz, PC_6H_4), 7.06-6.98 (m, 4H, PPh_2), 6.96-6.95 (m, 2H, NPh), 6.92-6.84 (m, 6H), 6.79-6.74 (m, 1H, PC_6H_4), 4.38-4.36 (m, 2H, COD), 4.16-4.13 (m, 2H, COD), 2.60-2.50 (m, 2H, COD), 2.46-2.36 (m, 2H, COD), 2.11-2.02 (m, 2H, COD), 1.98-1.91 (m, 2H, COD). $^{13}C\{^{1}H\}$ NMR (75.5MHz, C_6D_6) δ: 174.5-173.5 (d, $^{1}J_{Rh-C}$=40Hz, PC_6H_4), 148.1 (d, $^{2}J_{P-C}$=4Hz, NPh), 140.1 (s, PC_6H_4), 133.1 (d, $^{2}J_{P-C}$=9Hz, PPh_2), 131.6 (s), 129.9 (s, PPh_2), 129.7 (s, PC_6H_4), 129.4 (s, PC_6H_4), 129.3 (s), 128.5 (s), 123.4 (s), 122.9 (s), 93.4 (d, $^{1}J_{Rh-C}$=7Hz, COD), 68.9 (d, $^{1}J_{Rh-C}$=15Hz, COD), 32.5 (s, COD), 30.7 (s, COD). $^{31}P\{^{1}H\}$ NMR (202.5MHz, C_6D_6) δ: 46.4 (d, $^{2}J_{Rh-P}$=10

Hz). Anal. Calc'd for $C_{32}H_{31}PNRh$: C, 68.21; H, 5.55, N, 2.49. Found: C, 68.27; H, 5.71; N, 2.67.

Synthesis of [Rh(*o*-$C_6H_4PPh_2NPh$)(CH_2-*o*-$C_6H_4PPh_2NPh$)(μ-Cl)$_2$Rh(COD)] 48

[RhCOD(*o*-$C_6H_4PPh_2NPh$)](0.098 g, 0.17 mmol) was dissolved in CH_2Cl_2 (10 mL). The yellow solution was heated at reflux for 24h, during which time the solution became orange in colour. The solvent was removed *in vacuo*, and the product was recrystallized in benzene/CH_2Cl_2. Yield: 0.18 g (94%). ^{1}H NMR (500 MHz, C_6D_6) δ: 8.42-8.38 (br, 2H, PC_6H_4), 7.97 (dd, 1H, $^3J_{Rh-H}$=8Hz, $^4J_{P-H}$=3Hz, PC_6H_4), 7.92-7.87 (m, 4H, PPh_2), 7.84-7.79 (m, 2H, PC_6H_4), 7.69-7.65 (m, 3H, PC_6H_4), 7.53-7.45 (m, 4H, PPh_2), 7.28 (t, 2H, $^3J_{H-H}$=7Hz, NPh), 7.13-6.83 (m, 16H), 6.76-6.68 (m, 4H, NPh), 4.23 (dd, 2H, $^2J_{Rh-H}$=10Hz, $^4J_{P-H}$=4Hz, $RhCH_2$), 4.11 (m, 2H, COD), 3.79 (m, 2H, COD), 2.26-2.21 (m, 4H, COD), 1.37-1.33 (m, 4H, COD). ^{13}C{^{1}H}NMR (75.5 MHz, C_6D_6) δ: 170.7 (m, PC_6H_4), 157.9 (s, NPh), 150.9 (s, PPh_2), 148.9 (s, PC_6H_4), 138.1 (s), 137.9-134.8 (m, PPh_2), 134.7 (s, PC_6H_4), 134.1 (s, PC_6H_4), 133.1-132.9 (m, PPh_2), 132.7 (s), 131.6-131.5 (m, PC_6H_4), 130.8 (s), 130.5 (s, NPh), 125.0 (s), 124.6 (s), 122.9 (s), 122.1 (s), 121.6 (s), 78.3 (d, $^1J_{Rh-C}$=14Hz, COD), 76.6-76.0 (dd, $^1J_{Rh-C}$=32Hz, $^3J_{P-C}$=14Hz, $RhCH_2$), 31.3 (s, COD), 30.9 (s, COD). ^{31}P{^{1}H}NMR (121.5 MHz, C_6D_6) δ: 43.8 (d, $^2J_{Rh-P}$=12 Hz), 27.1 (d, $^2J_{Rh-P}$=3 Hz). Anal. Calc'd for $C_{57}H_{52}P_2N_2Cl_2Rh_2$: C, 62.03; H, 4.75; N, 2.54. Found: C, 58.09; H, 5.35; N, 1.78.

Synthesis of [Rh(*o*-$C_6H_4PPh_2NPh$)($Ph_2PCH_2CH_2PPh_2$)] 52

A solution of 1,2-*bis*(diphenylphosphino)ethane (DIPHOS) (0.04g, 0.07mmol) in THF (5 mL) was added dropwise at RT to [RhCOD(*o*-$C_6H_4PPh_2NPh$)] (0.03g, 0.08mmol) in the same solvent (5 mL). The mixture was stirred overnight at RT, after which time the solvent was removed *in vacuo*. The resulting solid was washed with benzene to remove excess DIPHOS, and was subsequently dried *in vacuo*. Yield: 0.03g (51%). ^{1}H NMR (500 MHz, C6D6) δ: 8.03-7.99 (m, 4H, DIPHOS-PPh_2, 7.74 (br, 1H, PC_6H_4), 7.57-7.53 (m, 4H, PPh_2), 7.51-7.48 (m, 4H, DIPHOS-PPh_2), 7.08-7.02 (m, 15H), 6.99-6.93 (m, 6H), 6.82 (t, 1H, $^3J_{H-H}$=7Hz, PC_6H_4), 6.70 (q, 1H, $^3J_{P-H}$=13Hz, $^3J_{H-H}$=6Hz, PC_6H_4), 6.56-6.53 (m, 2H, NPh), 6.48-6.45 (m, 1H, $^3J_{H-H}$=7Hz, PC_6H_4), 1.93-1.83 (m, 2H, $^2J_{P-H}$=26Hz, $^3J_{H-H}$=7Hz, DIPHOS-CH_2), 1.73-1.64 (m, 2H, $^2J_{P-H}$=25Hz, $^3J_{H-H}$=7Hz, DIPHOS-CH_2). ^{13}C{^{1}H}NMR (75.5 MHz, C_6D_6) δ: 153.9 (s, PC_6H_4), 146.3 (s), 144.6 (s), 142.2 (m, DIPHOS-C_6H_5), 138.6 (d, $^2J_{P-C}$=24 Hz, DIPHOS-C_6H_5), 137.9 (d, $^2J_{P-C}$=23 Hz, DIPHOS-C_6H_5), 134.4 (d, $^1J_{P-C}$=33 Hz, PPh_2), 133.6 (d, $^2J_{P-C}$=11 Hz, PPh_2), 132.5 (s), 131.4 (s), 130.9 (s), 128.7 (s), 126.2 (d, $^2J_{P-C}$=13 Hz, PC_6H_4), 123.5 (s), 121.1 (d, $^2J_{P-C}$=15 Hz, NPh), 119.2 (s, NC_6H_5), 32.1 (m, DIPHOS-CH_2), 29.4 (m, DIPHOS-CH_2). ^{31}P{^{1}H}NMR (202.5 MHz, C_6D_6) δ: 74.9 (dd, $^1J_{Rh-P}$=209Hz, $^3J_{P-P}$=24Hz), 57.2 (ddd, $^1J_{Rh-P}$=121Hz, $^3J_{P-P}$=24Hz), 24.1 (dd, $^2J_{Rh-P}$=22Hz, $^3J_{P-P}$=11Hz). Anal. Calc'd for $C_{48}H_{43}P_3NRh$: C, 69.49; H, 5.22; N, 1.69. Found: C, 69.75; H, 5.38; N, 1.55.

Synthesis of [IrCOD(*o*-$C_6H_4PPh_2NPh$)] *53*

A mixture of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$·Et_2O (0.25g, 0.30mmol) and [IrCl(COD)]$_2$ (0.09g, 0.14mmol) was dissolved in THF (5 mL) at RT. The homogeneous reddish solution was stirred overnight, after which time the solvent was removed *in vacuo*. The residue was washed with pentane and recrystallized in THF. Yield: 0.06g (67%). ^{1}H NMR (300MHz, C_6D_6) δ: 7.86 (d, 1H, $^3J_{P-H}$=9Hz, PC_6H_4), 7.60-7.53 (m, 4H, PPh_2), 7.30-7.25 (m, 1H, $^3J_{H-H}$=7Hz, PC_6H_4), 7.11-7.07 (m, 2H, NPh), 6.98-6.90 (m, 6H), 6.87-6.81 (m, 4H, PPh_2), 6.78-6.73 (m, 1H, PC_6H_4), 3.99-3.82 (m, 4H, COD), 2.61-2.35 (m, 4H, COD), 1.99-1.82 (m, 4H, COD). ^{13}C{^{1}H} NMR (75.5MHz, C_6D_6) δ: 172.9 (s, PC_6H_4), 146.3 (s, NPh), 140.9 (s), 135.5 (s, PC_6H_4), 133.2 (d, $^2J_{P-C}$=9Hz, PPh_2), 133.1 (s), 130.4 (s, PC_6H_4), 130.1 (s), 129.8 (s), 129.5 (s, NPh), 124.3 (s), 123.9 (s, PC_6H_4), 77.8 (s, COD), 52.7 (s, COD), 33.3 (s, COD), 31.4 (s, COD). ^{31}P{^{1}H} NMR (121.5MHz, C_6D_6) δ: 57.7. Anal. Calc'd for $C_{32}H_{31}PNIr$: C, 58.88; H, 4.79; N, 2.15. Found: C, 58.69; H, 4.77; N, 2.05.

X-Ray Structure Determinations of *36*, *44*, *45*, *46*·C_4H_8O, *47*, *48*·2 C_6H_6 and *53*

Data were collected at room temperature. No crystal decay was observed for any of the compounds. The resulting crystallographic values are given in Tables 2.1 and 2.2. ORTEP drawings of ***36***, ***44***, ***45***, ***46***·C_4H_8O, ***47***, ***48***·2 C_6H_6 and ***53*** are shown in Figures 2.3, 2.6-2.9, 2.11 and 2.15 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the captions for Figure 2.3, 2.6-2.9, 2.11 and 2.15 respectively.

Table 2.1: Crystallographic Parameters for 36, 44 and 45

	36	**44**	**45**
Formula	$C_{26}H_{24}$ NP	$C_{34}H_{35}NPRh$	$C_{38}H_{43}NPRh$
Formula weight	381.43	591.51	647.61
a (Å)	9.626(5)	10.122(6)	9.927(5)
b (Å)	12.325(7)	20.056(11)	11.193(6)
c (Å)	17.721(9)	14.533(8)	15.544(8)
α (°)	90	90	89.621(10)
β (°)	92.604(10)	107.315(11)	85.158(9)
γ (°)	90	90	72.044(10)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
Volume (Å^3)	2100.4(19)	2817(3)	1636.7(15)
D_{calc} (gcm^{-1})	1.206	1.395	1.314
Z	4	4	2
Abs coeff, μ, mm^{-1}	0.142	0.686	0.597
Temp (K)	293(2)	293(2)	293(2)
F(000)	808	1224	676
θ range (°)	2.01 - 23.22	2.03 - 23.22	1.31 - 23.32
Refl collected	8772	11910	7044
R_{int}	0.0269	0.0228	0.0134
Data $F_o^2>3\sigma(F_o^2)$	2984	4022	4656
Parameters	253	334	370
R^a (%)	0.0425	0.0238	0.0246
$R_w{}^a$ (%)	0.1285	0.0608	0.0637
Peak, hole (e-Å^{-3})	0.362, -0.308	0.252, -0.520	0.443, -0.388
Goodness of fit	1.030	1.060	1.029

$$^aR = \sum ||F_o| - |F_c|| / \sum |F_o|,\ R_w = [\sum(|F_o| - |F_c|)^2| / \sum |F_o|^2]^{0.5}$$

Table 2.2: Crystallographic Parameters for 46·C_4H_8O, 47, 48·2 C_6H_6 and 53

	46 · C_4H_8O	**47**	**48** · 2 C_6H_6	**53**
Formula	$C_{38}H_{43}NOPRh$	$C_{32}H_{31}NPRh$	$C_{69}H_{64}Cl_2N_2P_2Rh_2$	$C_{32}H_{31}NPIr$
Formula weight	663.61	563.46	1259.88	652.75
a (Å)	21.924(12)	9.835(5)	10.871(6)	9.826(5)
b (Å)	15.092(8)	11.331(6)	12.726(7)	11.278(5)
c (Å)	10.022(5)	12.325(7)	22.878(12)	12.306(6)
α (°)	90	79.137(10)	96.295(10)	79.013(8)
β (°)	95.361(10)	88.477(10)	98.239(10)	88.295(8)
γ (°)	90	77.591(10)	99.031(9)	77.195(9)
Crystal system	Moniclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	P-1	P-1	P-1
Volume ($Å^3$)	3301(3)	1317.3(12)	3065(3)	1305.3(11)
D_{calc} (gcm^{-1})	1.335	1.421	1.365	1.661
Z	4	2	2	2
Abs coeff,μ, mm^{-1}	0.596	0.730	0.720	5.197
Temp (K)	293(2)	293(2)	293(2)	293(2)
F(000)	1384	580	1292	644
θ range (°)	1.64 - 23.20	1.87 - 23.24	2.26 - 23.31	2.51 - 23.26
Refl collected	13757	5641	13036	5508
R_{int}	0.0184	0.0149	0.0400	0.0270
Data $F_o^2>3\sigma(F_o^2)$	4692	3739	8682	3712
Parameters	379	316	694	316
R^a (%)	0.0257	0.0255	0.0567	0.0313
$R_w{}^a$ (%)	0.0653	0.0700	0.1402	0.0799
Peak, hole($e^-Å^{-3}$)	0.294, -0.317	0.404,-0.460	1.434, -0.789	1.164, -2.361
Goodness of fit	1.029	1.006	1.036	1.042

$$^aR = \sum ||F_o| - |F_c|| / \sum |F_o|,\ R_w = [\sum(|F_o| - |F_c|)^2| / \sum |F_o|^2]^{0.5}$$

2.3 Results and Discussion

The focus of this research has been the synthesis of late transition metal containing phosphinimine complexes. A series of rhodium phosphinimine (Ph_3PNR_{aryl}) complexes with various substituents on the imine nitrogen phenyl ring (**44-47**) were prepared. Different substituents could be introduced on the ligand from the use of various substituted phenyl azides, which are in turn, synthesized from modification of several different literature preparations.[180,181] Most previously reported syntheses of phenyl azides suffer from low yields and the presence of impurities, however, when a diazonium tetrafluoroborate salt is generated as the intermediate, the reaction proceeds smoothly.[178] Subsequent nucleophilic displacement with an azide anion forms **33-35** in high yields (Figure 2.1).

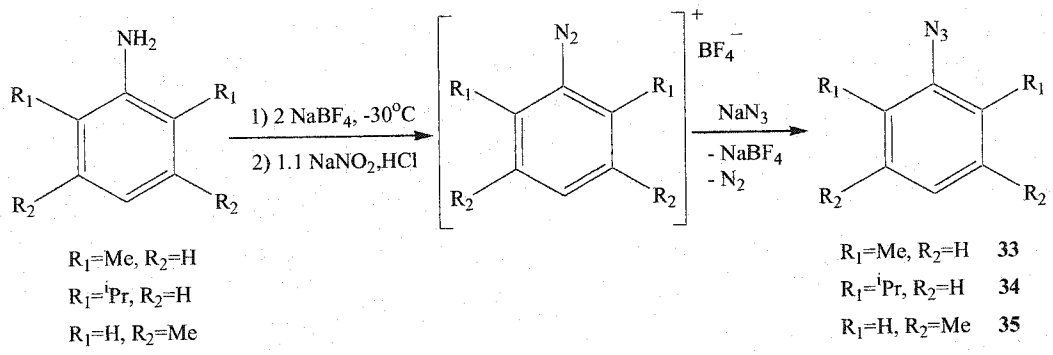
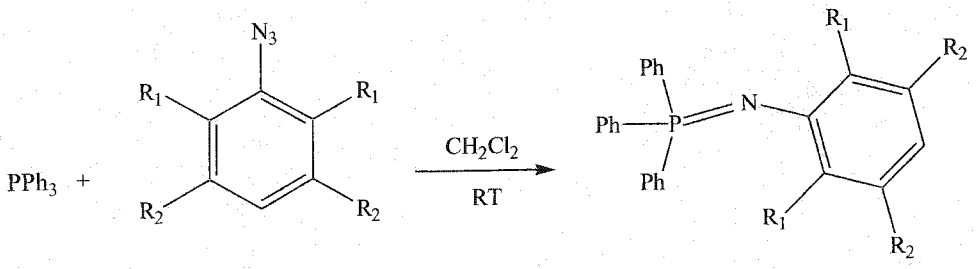


Figure 2.1 Synthesis of 2,6- or 3,5-disubstituted phenyl azide

The phosphinimine ligands **36-38** were synthesized upon oxidation of triphenylphosphine with the appropriate substituted phenyl azides **33-35** (Figure 2.2). The products were obtained in high yields after recrystallization. Upon oxidation, there is a slight upfield shift in the $^{31}P\{^1H\}$ NMR spectrum for

compounds **36** (-9.8 ppm) and **37** (-8.9 ppm) , and a slight downfield shift for compound **38** (-1.5 ppm) compared with free PPh_3 (-5.2 ppm). ^1H and $^{13}C\{^1H\}$ NMR spectroscopy showed evidence for the formation of the desired products. The X-ray structure of compound **36** is illustrated in Figure 2.3. Compound **36** was similar to triphenyl(phenylimino)phosphine **39**, except two methyl groups were introduced to the 2,6-position of the N-phenyl ring. The P=N distance of compound **36** (1.552(2) Å) was shorter than the analogous distance in Ph_3PNPh (1.602(3) Å). The N-C_{aryl} bond distance of compound **36** (1.406(3) Å) was significantly longer than the N-C_{aryl} distance in Ph_3PNPh (1.330(5) Å). The P-N-C_{aryl} bond angle of Ph_3PNPh (130.4(3)°) was smaller than P(1)-N(1)-C(19) angle of **36** (132.23(17)°). The elongation of the N-C_{aryl} bond and the larger P-N-C angle in **36** is likely due to the introduction of the *ortho*-methyl groups in where the aryl ring was required to bent further away to compensate the steric interaction.



R_1=Me, R_2=H **33**
R_1=^{i}Pr, R_2=H **34**
R_1=H, R_2=Me **35**

R_1=Me, R_2=H **36**
R_1=^{i}Pr, R_2=H **37**
R_1=H, R_2=Me **38**

Figure 2.2 Synthesis of 2,6- or 3,5-disubstituted phosphinimine ligands

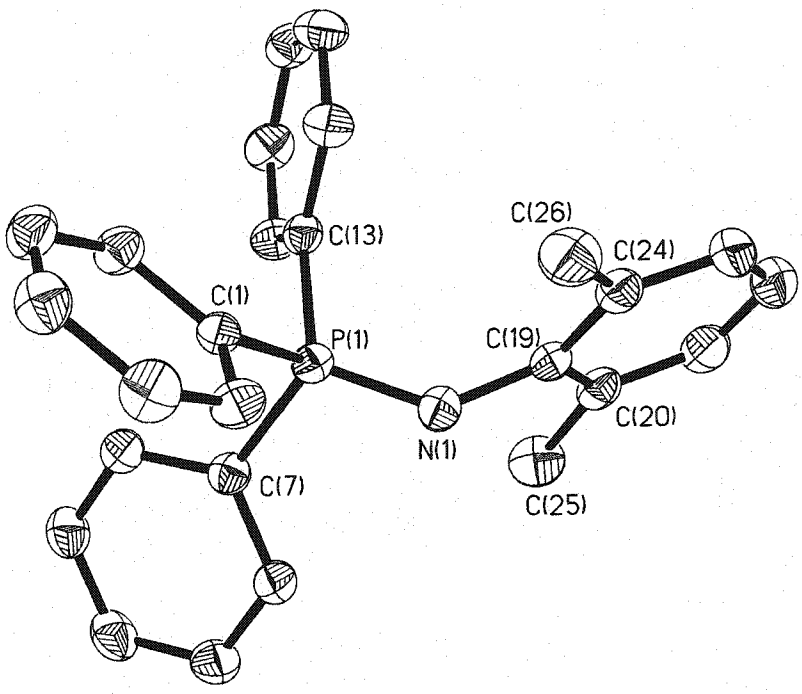


Figure 2.3 ORTEP drawing of **36,** 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: P(1)-C(1) 1.825(2) Å, P(1)-C(13) 1.823(2) Å, P(1)-N(1) 1.552(2) Å, N(1)-C(19) 1.406(3) Å; P(1)-N(1)-C(19) 132.23(17)°

Lithiation of triphenyl(phenylimino)phosphine, Ph_3PNPh **39**, was achieved employing a literature method.[179] Reacting Ph_3PNPh with LiPh generated the *ortho*-metallated species $[Li(o\text{-}C_6H_4PPh_2NPh)]_2 \cdot Et_2O$ **43** in 47% yield. Lithiation of substituted aryl phosphinimines (**36-38**) were performed by a modified method, where LiMe or Li^{n}Bu was used instead of LiPh. Depending on the size of the N-aryl substituents, longer reaction times were required

(Figure 2.4). All lithiated intermediates showed a downfield resonance in $^{31}P\{^{1}H\}$ spectrum, indicating the coordination of lithium metal to the phosphinimine ligand. The ^{1}H NMR spectrum showed that deprotonation at the *ortho* position of one phenyl ring had occurred. This species likely has a structure similar to an analogous compound reported by Steiner *et al.*, where they reacted $Ph_3PNSiMe_3$ with LiMe,[159] forming the dimeric organolithium complex $[Li(o\text{-}C_6H_4PPh_2NPh)]_2 \cdot Et_2O$. Exhaustive attempts to obtain X-ray quality crystals of compounds **40–43** were unsuccessful.

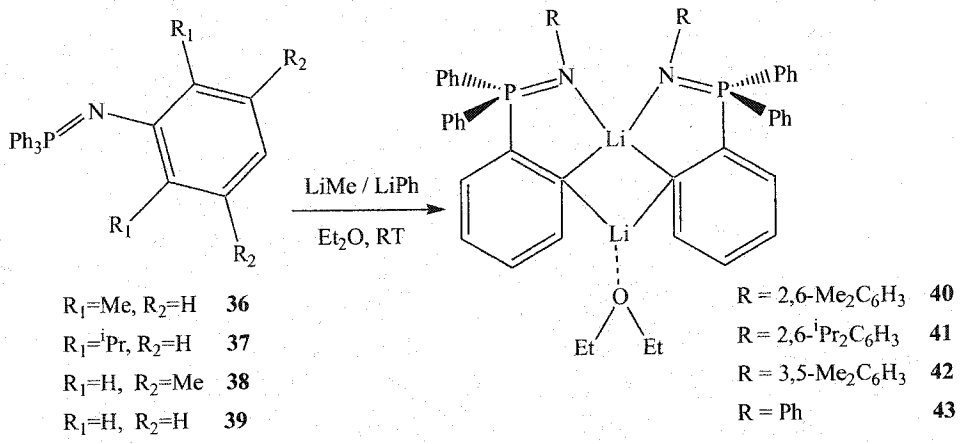


Figure 2.4 Lithiation of substituted phosphinimine ligands

The *ortho*-metallated species **40-43** all had the requirements of an organometallic ligand capable of side arm donation. The deprotonated *ortho* phenyl carbon atom is able to form a rhodium-carbon σ-bond in a transmetallation reaction with the chloro(1,5-cyclooctadiene)rhodium(I) dimer, forming the monomeric rhodium(I) organometallic complexes **44-47** (Figure 2.5). In addition, the nitrogen atom from the Ph_2PNR unit acts as a side-arm

donating group through donation of an electron pair to the rhodium center, thus providing further stability to the monomeric complexes.

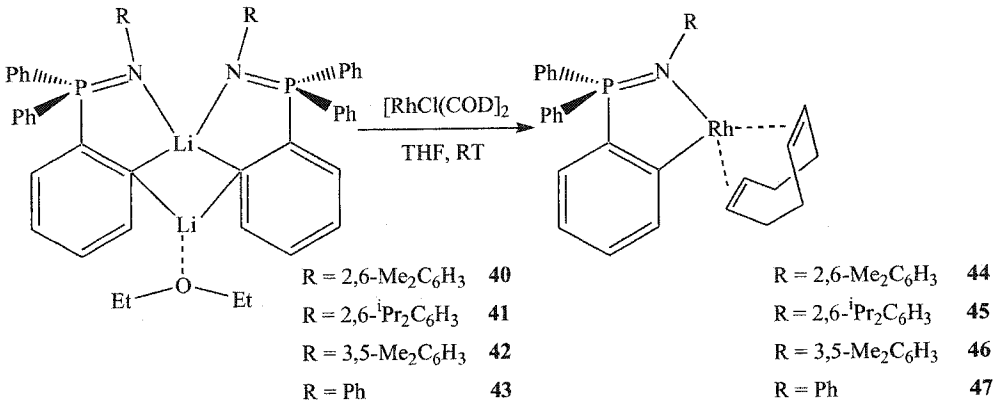


Figure 2.5 Synthesis of rhodium(I) phosphinimine complexes **44–47**

Complexes **44–47** were synthesized in good yield by treating [RhCl(COD)]$_2$ with the appropriate organolithium intermediates **40–43** in THF at room temperature. All complexes were characterized by a variety of techniques, such as ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy, elemental analyses and X-ray diffraction studies. While comparing all rhodium(I) metal complexes **44–47**, there was an upfield shift in the ^{31}P{^{1}H} spectrum when steric bulk was introduced to the 2,6-positions of the imine phenyl ring. When the N-phenyl ring was unsubstituted (compound **47**), the ^{31}P{^{1}H} NMR had a signal at 46.4 ppm. When the N-phenyl ring was substituted by two methyl groups at 2,6-positions (compound **44**), the ^{31}P{^{1}H} signal shifted further upfield to 43.3 ppm. Whereas when the N-phenyl ring was substituted by two more bulky isopropyl groups at 2,6-positions (compound **45**), the ^{31}P{^{1}H} signal shifted to 39.9ppm. In contrast, if steric bulk was introduced to the 3,5-positions of the imine phenyl ring as in compound **46**, the ^{31}P{^{1}H} shift remained very similar to

the unsubstituted compound **47**. The rhodium-bound aryl carbon gave rise to a doublet in the $^{13}C\{^1H\}$ NMR in the range of 170–180 ppm ($^1J_{Rh-C}$ typically 40 Hz), confirming that the rhodium atom was bound directly to the aryl ring of the phosphinimine ligand. ^1H NMR studies unambiguously showed the formation of compounds **44–47**. The ^1H NMR spectra of all four species showed distinct methylene and methine protons of the cyclooctadiene(COD) ligand due to the dissymmetry of the metallated phosphinimine ligand. A NOESY NMR experiments unambiguously confirmed that the upfield methylene and methine signals are assigned to those *trans* to the aryl-carbon. Crystals of **44 - 47** suitable for X-ray structural determination were grown from a mixture of THF/Et_2O or THF/C_6D_6 solvents. The X-ray structures of compounds **44 - 47** are illustrated in Figures 2.6 – 2.9. X-ray structures of compounds **44 - 47** were very similar. All exhibited a Rh-C σ bond and a Rh←N donor bond, in addition to a coordinated cyclooctadiene ligand, thus generating a monomeric, slightly distorted square planar, 4-coordinate Rh complex with bite angles at the Rh center (N-Rh-C) of 85.12(9)° (compound **44**), 85.49(9)° (compound **45**), 85.10(9)° (compound **46**), and 84.77(9)° (compound **47**). They also feature a five-membered metallocycle containing four different atom types incorporating the P=N bond. The metallocyclic ring was essentially planar and the phenyl ring attached to the Rh metal was almost co-planar with the metallocycle. The N-phenyl ring was twisted away from co-planarity with respect to the metallocyclic ring. This presumably arose from the steric interaction of the phosphinimine ligand with the cyclooctadiene ligand on the Rh metal center. This resulted in a lengthening of the N-C_{phenyl} distance in the rhodium metallated compound **44**

(1.445(3) Å) relative to the free ligand **36** (1.406(3) Å). Similar phenomenon were also observed in the structure of [RhCOD(*o*-$C_6H_4PPh_2NPh$)] **47** (1.450(3) Å) compared to the free ligand Ph_3PNPh (1.330(5) Å).[182] When comparing the P=N distance of compound **36** (1.552(2) Å) with the rhodium coordinated compound **44** (1.614(2) Å), bond lengths are significantly different. Since two methyl groups were introduced to the 2,6-positions of the N-phenyl ring, additional steric bulk was applied between the metallocyclic ring and the N-phenyl ring. Therefore, lengthening of the P=N bond was required to reduced steric strain. Conversely, the P=N bond length did not alter observably between the free Ph_3PNPh (1.602(3) Å) and the rhodium complex **47** (1.609(2) Å). That the expected lengthening of the P=N bond upon coordination to the rhodium center was not observed in this case might be due to the compensation of twisting of the phenyl group out of the plane. Therefore, it was the N-C bond that lengthened, rather then the P=N bond that changed. The Rh-C(1) bond length of compound **44** (2.065(3) Å), compound **45** (2.058(3) Å), compound **46** (2.068(3) Å), and compound **47** (2.069(3) Å) were comparable to other complexes containing Rh-C_{aryl} bonds. For example: 2.049(6) Å in Rh(CH_2-$PhCF_3$)[$C_6H(CH_3)_2(CH_2PPh_2)_2$]I[183] or 2.079(3) Å in RhCp*(C_6F_5)(PMe_3)I.[184]

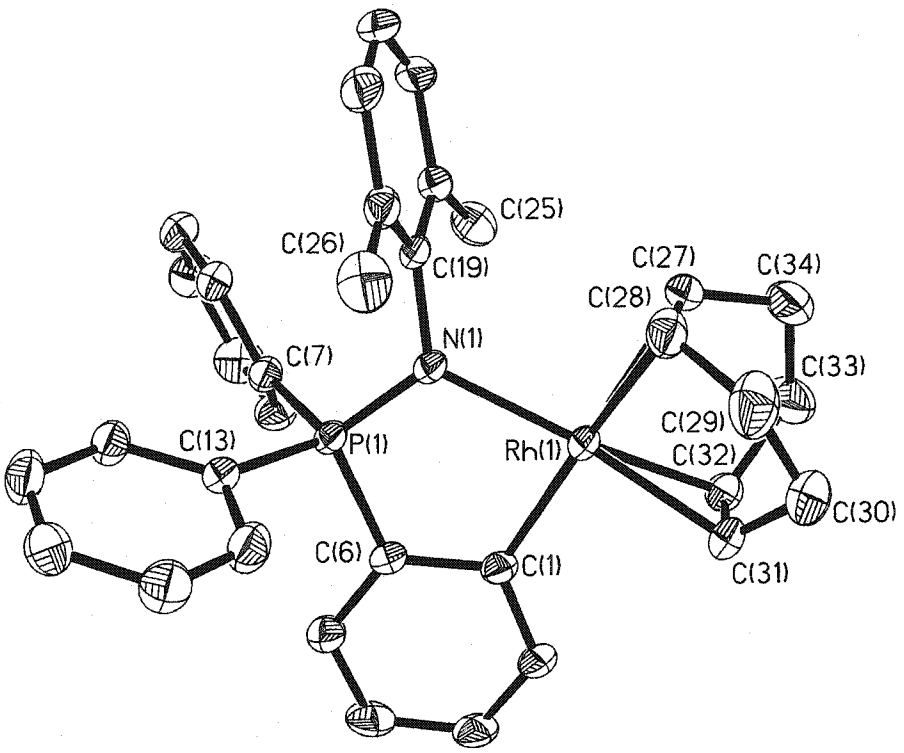


Figure 2.6 ORTEP drawing of **44**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.125(2) Å, Rh(1)-C(1) 2.065(3) Å, P(1)-N(1) 1.614(2) Å, N(1)-C(19) 1.445(3) Å, Rh(1)-C(27) 2.233(3) Å, Rh(1)-C(28) 2.213(3) Å, Rh(1)-C(31) 2.112(3) Å, Rh(1)-C(32) 2.089(3) Å; N(1)-Rh(1)-C(1) 85.12(9)°, P(1)-N(1)-Rh(1) 115.84(10)°, C(19)-N(1)-Rh(1) 123.96(16)°, C(27)-Rh(1)-C(32) 81.06(11)°, C(28)-Rh(1)-C(31) 80.95(12)°.

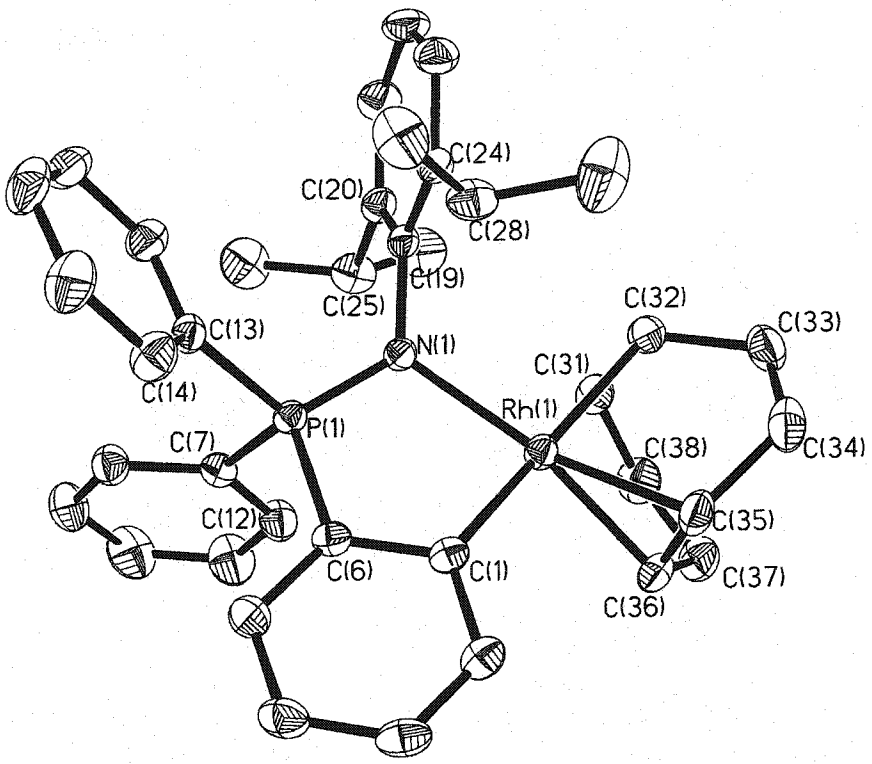


Figure 2.7 ORTEP drawing of **45**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.141(2) Å, Rh(1)-C(1) 2.058(3) Å, P(1)-N(1) 1.605(2) Å, N(1)-C(19) 1.440(3) Å, Rh(1)-C(31) 2.183(3) Å, Rh(1)-C(32) 2.220(3) Å, Rh(1)-C(35) 2.102(3) Å, Rh(1)-C(36) 2.116(3) Å; N(1)-Rh(1)-C(1) 85.49(9)°, P(1)-N(1)-Rh(1) 112.43(11)°, C(19)-N(1)-Rh(1) 124.01(17)°, C(31)-Rh(1)-C(36) 81.31(12)°, C(32)-Rh(1)-C(35) 80.96(12)°.

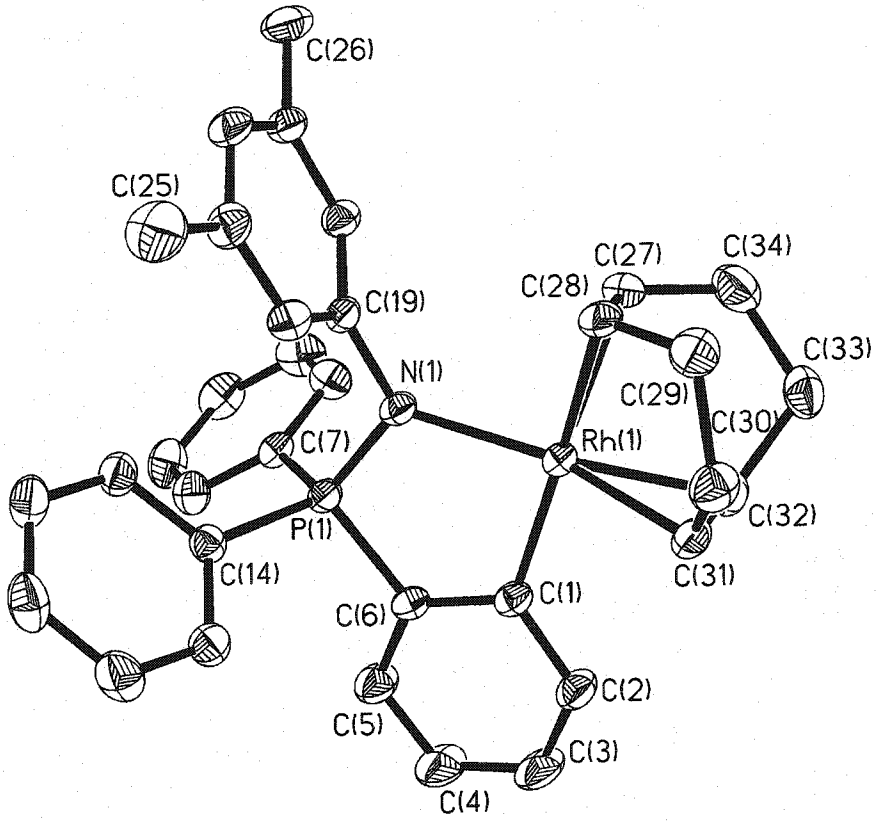


Figure 2.8 ORTEP drawing of **46**, 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized THF molecule have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.108(2) Å, Rh(1)-C(1) 2.068(3) Å, P(1)-N(1) 1.617(2) Å, N(1)-C(19) 1.454(3) Å, Rh(1)-C(27) 2.200(3) Å, Rh(1)-C(28) 2.235(3) Å, Rh(1)-C(31) 2.090(3) Å, Rh(1)-C(32) 2.107(3) Å; N(1)-Rh(1)-C(1) 85.10(9)°, P(1)-N(1)-Rh(1) 115.78(11)°, C(19)-N(1)-Rh(1) 124.54(17)°, C(27)-Rh(1)-C(32) 81.47(11)°, C(28)-Rh(1)-C(31) 81.02(11)°.

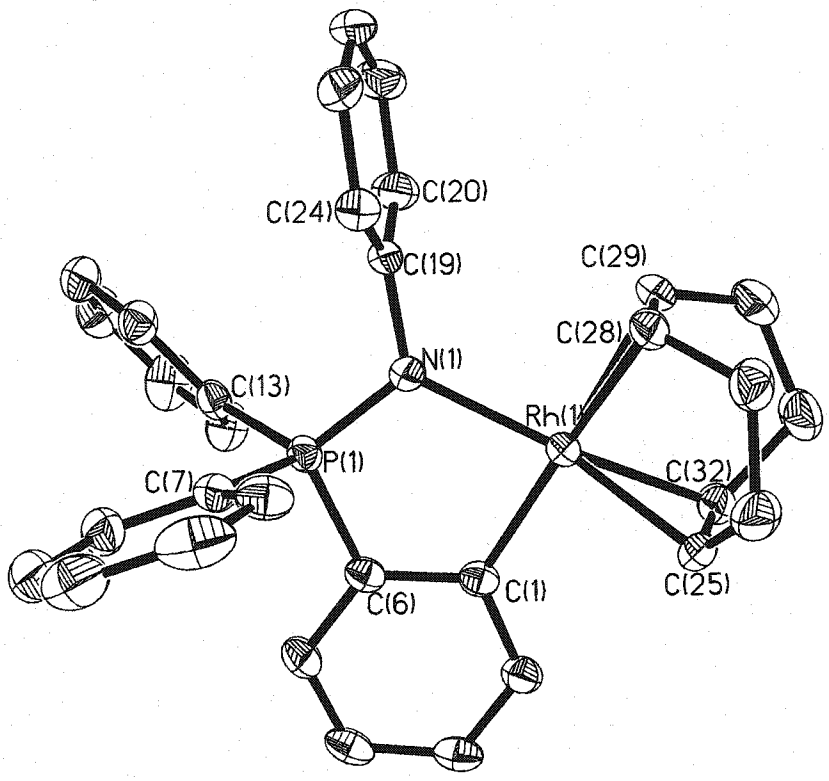
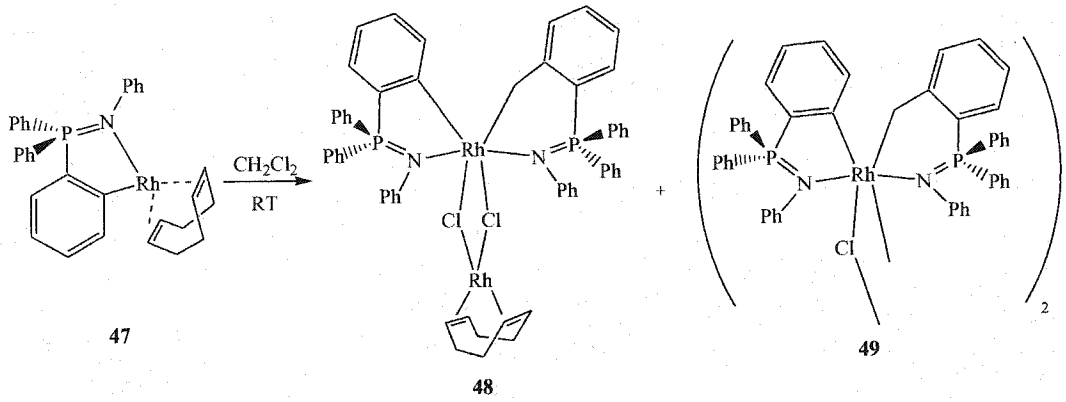


Figure 2.9 ORTEP drawing of **47**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Rh(1)-N(1) 2.112(2) Å, Rh(1)-C(1) 2.069(3) Å, P(1)-N(1) 1.609(2) Å, N(1)-C(19) 1.450(3) Å, Rh(1)-C(25) 2.095(3) Å, Rh(1)-C(32) 2.104(3) Å, Rh(1)-C(28) 2.225(3) Å, Rh(1)-C(29) 2.207(3) Å; N(1)-Rh(1)-C(1) 84.77(9)°, P(1)-N(1)-Rh(1) 115.33(12)°, C(19)-N(1)-Rh(1) 126.31(16)°, C(25)-Rh(1)-C(28) 80.98(11)°, C(32)-Rh(1)-C(29) 81.20(11)°.

Yellow crystals of [RhCOD(*o*-$C_6H_4PPh_2NPh$)] **47** were recrystallized from THF/Et_2O. However, it was unexpected that a solution of compound **47** in methylene chloride slowly transformed to other compounds. These new compounds were formed in essentially quantitative yields after stirring in CH_2Cl_2 for a couple of days. X-ray crystallographic study of compound **48** demonstrated that the orange coloured, binuclear Rh(I)-Rh(III) complex had formed (Figure 2.11). This complex consisted of two phosphinimine ligands with a methylene group inserted into one of the Rh-C_{aryl} bonds, generating a five as well as a six-membered metallacycle. The binuclear structure was apparent with two rhodium centers joined by two bridging chloride ligands. The geometry of the Rh(III) center was pseudo-octahedral, where both nitrogen atoms occupied the axial position with an almost linear N(1)-Rh(1)-N(2) angle of 176.90(18)°. A cyclooctadiene ligand was coordinated to the Rh(I) center, generating a slightly distorted square planar geometry with a bite angle at the rhodium (I) center of 88.58(6)°. The Rh(1)-N(2) bond length (2.153(5) Å) in the six membered metallacycle was longer than Rh(1)-N(1) bond length (2.107(5) Å) in the five membered metallacycle. In the same manner, P(2)-N(2) bond length (1.616(5) Å) in the six membered metallacycle is also longer than the P(1)-N(1) bond length (1.602(5) Å) in the five membered metallacycle. The Rh(1)-Rh(2) distance of 3.647 Å demonstrated the absence of a Rh-Rh metal bond. While reacting compound **47** with CH_2Cl_2, two products (**48** and **49**) are present in solution. Compound **48** was the dominant species and compound **49** was the minor species (Figure 2.10). This transformation could be conveniently followed by $^{31}P\{^1H\}$ NMR spectroscopy. After compound **47** was stored in CH_2Cl_2

solution for a few hours, new resonances appeared in the $^{31}P\{^{1}H\}$ NMR spectrum, while peaks due to **47** slowly diminish. Within a few days, all traces of compound **47** were gone. Compound **48** showed two sets of resonances. A doublet centered at 43.7 ppm ($^{2}J_{Rh\text{-}P}$=12 Hz) was attributed to the phosphorus atom in the five-membered metallacycle, and another doublet centered at 27.1 ppm ($^{2}J_{Rh\text{-}P}$=3 Hz) was attributed to the phosphorus atom in the six-membered metallocycle. For compound **49**, a doublet centered at 34.6 ppm ($^{2}J_{Rh\text{-}P}$=11Hz) was attributed to the phosphorus atom in the five-membered metallocycle, while a singlet centered at 28.1 ppm was attributed to the phosphorus atom in the six-membered metallocycle.



47 **48** **49**

Figure 2.10 Reaction of **47** with methylene chloride

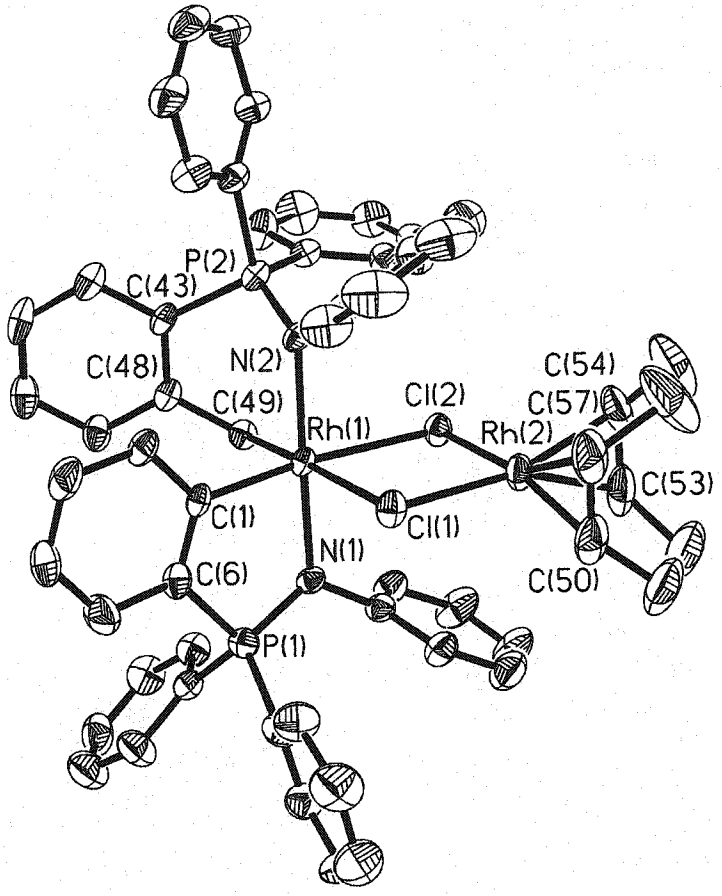


Figure 2.11 ORTEP drawing of **48**, 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized benzene molecule have been omitted for clarity. Selected bond distances and angles: Rh(1)-C(1) 2.005(6) Å, Rh(1)-C(49) 2.082(6) Å, Rh(1)-N(1) 2.107(5) Å, Rh(1)-N(2) 2.153(5) Å, Rh(1)-Cl(1) 2.566(2) Å, Rh(2)-C(53) 2.090(8) Å, Rh(2)-C(50) 2.090(8) Å, Rh(2)-C(54) 2.095(7) Å, Rh(2)-C(57) 2.113(9) Å, N(1)-P(1) 1.602(5) Å, N(2)-P(2) 1.616(5) Å, C(48)-C(49) 1.485(9) Å; C(1)-Rh(1)-C(49) 90.3(2)°, C(1)-Rh(1)-N(1) 84.4(2)°, C(49)-Rh(1)-N(2) 89.7(2)°, N(1)-Rh(1)-N(2) 176.90(18)°, C(53)-Rh(2)-C(50) 82.6(4)°, C(54)-Rh(2)-C(57) 83.9(4)°.

Triphenylphosphine (PPh_3) was reacted with the bi-nuclear Rh(I)-Rh(III) **48** (Figure 2.12). This reaction resulted in cleavage of the chloride bridge and coordination either to the Rh(I) or Rh(III) center, forming different mono-nuclear fragments. Possible reaction products are shown in Figure 2.12. Though multiple products were formed in this reaction, the $^{31}P\{^1H\}$ NMR spectrum revealed that the major product was compound **49** (d at 34.6 ppm ($^2J_{Rh-P}$=11Hz) and s at 28.1 ppm). It is likely that the PPh_3 did not coordinate strongly to the rhodium center; instead, it rearranged and formed the more stable rhodium(III) dimer **49**. Due to the very similar solubility of compounds **49-51**, attempts to isolate pure compound **49** were not successful.

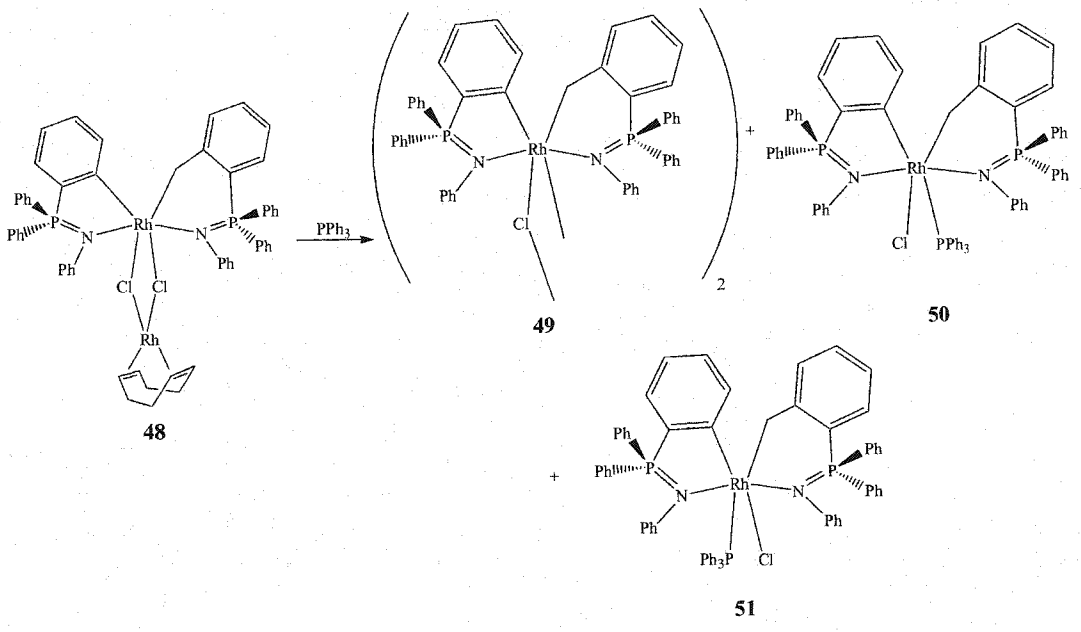
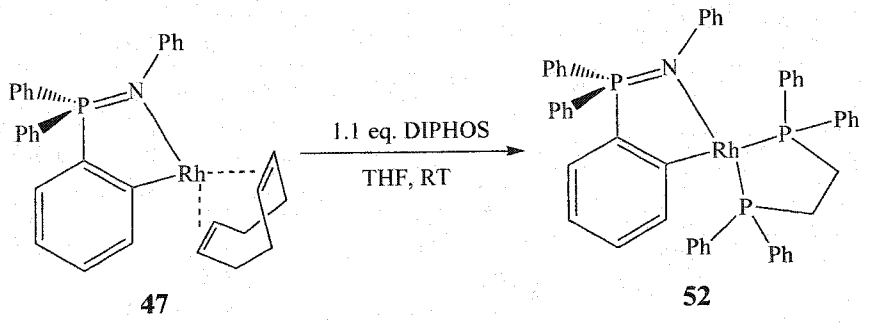


Figure 2.12 Reaction of compound **48** with PPh_3

Since insertion of the methylene group into the rhodium-aryl bond of compound **47** occurred, we tried to extend this chemistry to the more bulky N-

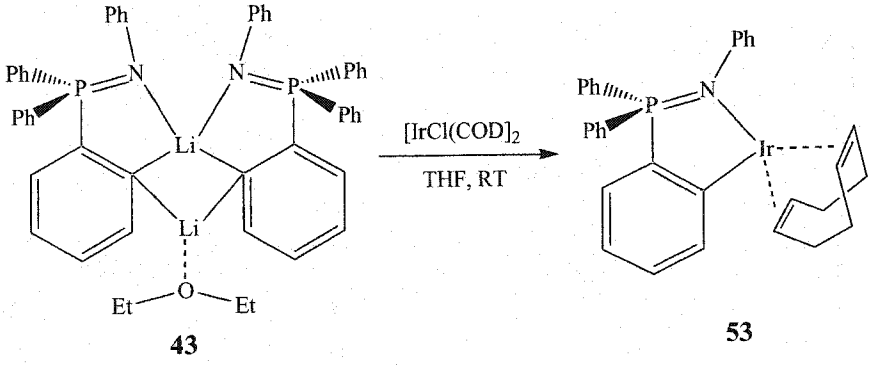
phenyl 2,6-disubstituted complexes **44** and **45**, and the N-phenyl 3,5-disubstituted complex **46**. For this purpose, compounds **44-46** were further purified by recrystallization or by precipitation from a saturated THF solution, then reacted with methylene chloride at room temperature. Interestingly, both N-phenyl 2,6-disubstituted complexes **44** and **45** did not react with methylene chloride even after prolonged stirring. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy showed no evidence for the formation of any new compound. In contrast, multiple products were formed while reacting the N-phenyl 3,5-disubstituted complex **46** with methylene chloride. $^{31}P\{^{1}H\}$ NMR showed the disappearance of the initial signal (46.8 ppm), and four new signals appeared within the range of 47- 28 ppm with varied intensities. Attempts to separate these products were unsuccessful. It seemed that when steric bulk was introduced to the 2,6-position of the N-phenyl ring (compounds **44** and **45**), it prevented oxidative addition of the methylene chloride to the rhodium center.

In order to further study the insertion of the methylene group into the rhodium-carbon bond, two tailor-made compounds, a rhodium and an iridium compound were synthesized. Compound **52** is analogous to compound **47**, having a more bulky chelated phosphine ligand, DIPHOS (1,2-*bis*(diphenylphosphinoethane)) coordinated to the rhodium center instead of a cyclooctadiene moiety (Figure 2.13). Compound **53** is also analogous to compound **47**, though with an iridium metal center (Figure 2.14).



47 52

Figure 2.13 Synthesis of compound **52**



43 53

Figure 2.14 Synthesis of compound **53**

Compound **52** was synthesized in moderate yield by reacting compound **47** with 1.1 equivalents of DIPHOS to displace the COD ligand on the rhodium center. Compound **52** was obtained pure by precipitating out of a saturated THF solution upon prolonged storage. Attempts to obtain X-ray quality crystals of compound **52** were unsuccessful; in fact, it was characterized by $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum showed three distinct signals: a doublet of doublets centered at 74.9 ppm, and a doublet of doublet of doublets centered at 57.2 ppm, which corresponded to the phosphorus atoms on the DIPHOS ligand, as well as a doublet of doublets centered at 24.1 ppm, corresponding to the phosphorus from the phosphinimine ligand.

Elemental analysis indicated that **52** has the empirical formula of [Rh(*o*-$C_6H_4PPh_2NPh$)($Ph_2PCH_2CH_2PPh_2$)].

Compound **53** was synthesized in moderate yield by reacting compound **43** with $[IrCl(COD)]_2$ in THF at room temperature (Figure 2.14). $^{31}P\{^1H\}$ spectroscopy showed a singlet centered at 57.7 ppm, whereas ^1H and $^{13}C\{^1H\}$ NMR spectroscopy as well as elemental analysis confirmed the formulation of compound **53**. Orange coloured plate-like X-ray quality crystals were obtained by slowly evaporating a concentrated THF solution of compound **53**. The ORTEP view of **53** is shown in Figure 2.15. Compound **53** was isostructural to compound **47** except with an iridium metal center. The X-ray analysis demonstrated that the iridium center has a slightly distorted square planar geometry. Compound **53** exhibited an Ir-C σ-bond and a Ir←N donor bond thereby forming a five-membered metallacycle. The metal center also contains a cyclooctadiene ligand thus forming a 4-coordinated iridium (I) complex with a bite angle of 84.77(19)° [C(1)-Ir(1)-N(1)], which is almost identical to the analogous bite angle found in the rhodium compound **47** (84.77(9)°). The imine phenyl ring was twisted and bent away from the COD ligand with an angle of 126.6(3)°, which is also found in compound **47** (126.31(16)°). The angles around the COD ligand: C(29)-Ir(1)-C(26) (80.7(2)°) and C(30)-Ir(1)-C(25) (81.3(2)°) were also relatively close to the analogous angles in compound **47**. While comparing the M-N bond lengths of compound **47** and **53**, the Rh(1)-N(1) bond length (2.112(2) Å), was longer than the analogous Ir(1)-N(1) bond length (2.081(5) Å).

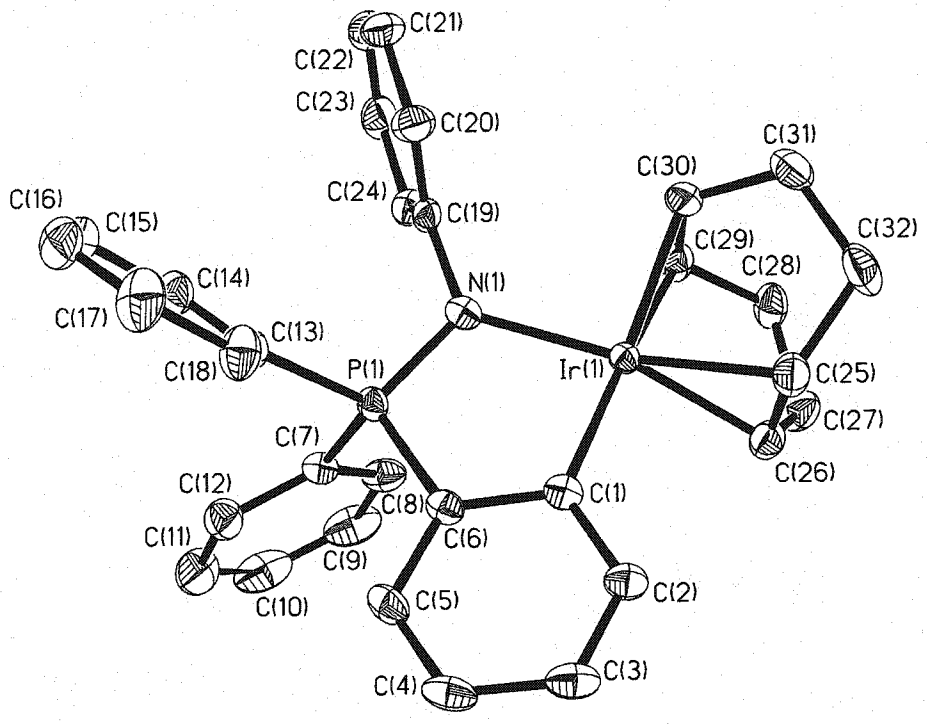


Figure 2.15 ORTEP drawing of ***53***, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles: Ir(1)-N(1) 2.081(5) Å, Ir(1)-C(1) 2.084(5) Å, P(1)-N(1) 1.628(5) Å, N(1)-C(19) 1.440(7) Å, Ir(1)-C(25) 2.104(6) Å, Ir(1)-C(26) 2.106(6) Å, Ir(1)-C(29) 2.195(6) Å, Ir(1)-C(30) 2.179(5) Å; N(1)-Ir(1)-C(1) 84.77(19)°, P(1)-N(1)-Ir(1) 115.8(3)°, C(19)-N(1)-Ir(1) 126.6(3)°, C(25)-Ir(1)-C(30) 81.3(2)°, C(26)-Ir(1)-C(29) 80.7(2)°.

Both compound **52** and compound **53** reacted with methylene chloride at room temperature. The proposed products for the reaction of compound **52** with CH_2Cl_2 are shown in Figure 2.16. Compound **54** showed 3 sets of signals in $^{31}P\{^1H\}$ NMR spectrum: a doublet of doublet of doublets centered at 57.5 ppm, and a doublet of doublets centered at 51.2 ppm which corresponded to the phosphorus atoms on the DIPHOS ligand. As well, a doublet centered at 30.0 ppm corresponding to the phosphorus atom from the phosphinimine ligand. A comparison of the $^{31}P\{^1H\}$ NMR spectrum of compound **54** with compound **52** showed that signals are relatively similar except for the doublet of doublets centered at 74.9 ppm (compound **52**), which was shifted significantly to 51.2 ppm. Due to the similarity of the $^{31}P\{^1H\}$ NMR spectra of these complexes, we proposed that a similar species has formed *via* oxidative addition of the C-Cl bonds followed by insertion of the CH_2 into the Rh-C_{aryl} bond.

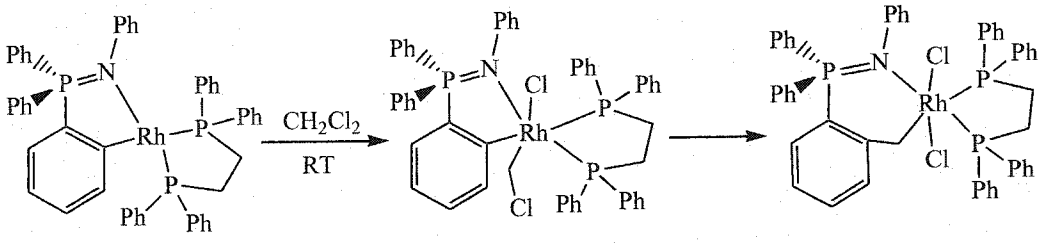


Figure 2.16 Proposed reaction of compound **52** with CH_2Cl_2

To further confirm a monomeric compound was formed in the case shown in Figure 2.16, compound **48** was reacted with 1.1 equivalents of DIPHOS in order to produce the binuclear compound **55** where the COD ligand was displaced by the DIPHOS ligand. The products of the reactions shown in Figure 2.16 and Figure 2.17 were compared. The $^{31}P\{^{1}H\}$ NMR spectrum showed that multiple products with signals ranging from 80 – 20 ppm were formed. Signals centered at 77.1 ppm (d, $^{1}J_{Rh-P}$=200Hz) and 73.1 ppm (d, $^{1}J_{Rh-P}$=199 Hz) indicated the formation of compounds **56** or **57**. These $^{31}P\{^{1}H\}$ NMR signals were confirmed by reacting the $[RhCl(COD)]_2$ with excess DIPHOS ligands. Also evident were signals centered at 34.7 ppm ($^{2}J_{Rh-P}$=10 Hz) and 28.1 ppm, indicated the formation of compound **49**. Another compound was present which had three signals: 74.1 ppm (d, $^{1}J_{Rh-P}$=198 Hz), 44.7 ppm (d, $^{2}J_{Rh-P}$=13 Hz) and 27.4 ppm suggesting the formation of compound **55** (Figure 2.17). Attempts to separate compounds **49**, **55**, **56** and **57** were unsuccessful. The different products formed in the reactions illustrated in Figure 2.16 and Figure 2.17 further suggest that compound **52** has likely underwent oxidative addition in order to form a monomeric rhodium (I) complex (compound **54**). The observations indicate the displacement of COD ligand in compound **47** with the DIPHOS ligand prevented the dimerization to form a species like compound **49** from occurring. This is likely due to the stronger Rh-P σ-bond which prohibited the dissociation of the DIPHOS ligand from the rhodium center, which prevents further rearrangement of compound **52**.

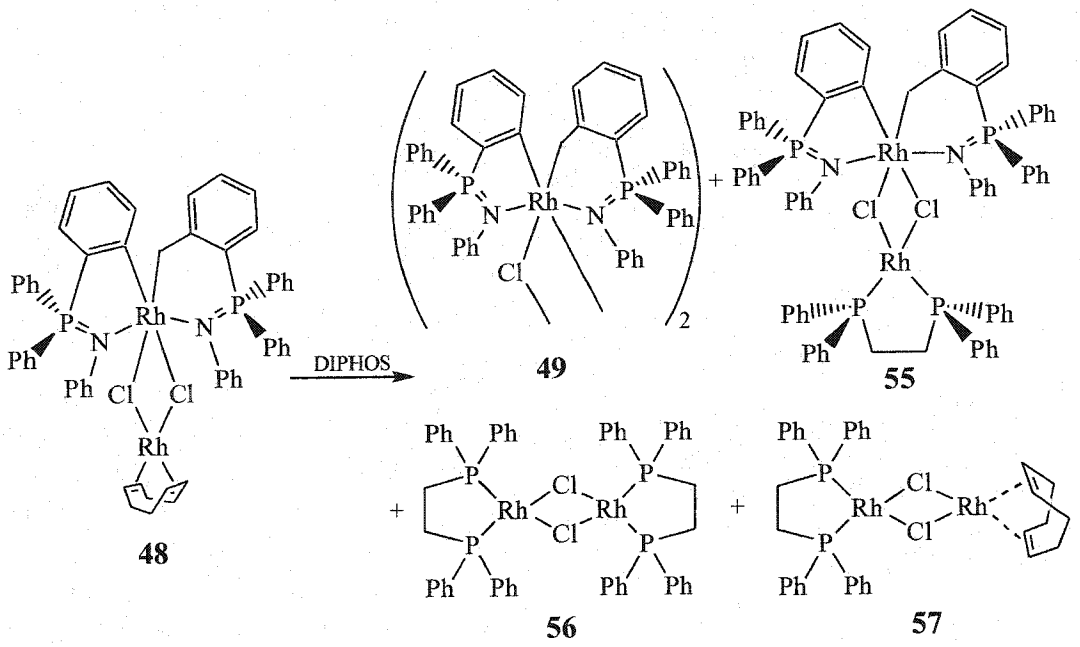


Figure 2.17 Ligand displacement reaction of compound **48** with DIPHOS

Similar reactions were performed with the iridium(I) compound ***53***. The colour of the reaction mixture changed from orange to yellow after prolonged stirring in methylene chloride. The $^{31}P\{^{1}H\}$ NMR showed the disappearance of the starting material signal and that multiple products had formed. Attempts to isolate single products were unsuccessful.

The ^{1}H NMR spectrum of both compounds ***52*** and ***53*** after reaction with CH_2Cl_2 were complicated. Resonances due to the inserted CH_2 group into the M-C_{aryl} bond were apparently obscured by other resonances. In order to confirm the insertion of the methylene group into the M-C_{aryl} bond, ^{2}D NMR experiments were performed. After prolonged stirring of compounds ***52*** and ***53*** in CD_2Cl_2, ^{2}D NMR spectra revealed the presence of a signal centered at 4.23 ppm for compound ***54***, and a signal centered at 4.25 ppm in product mixture

while reacting compound **53** with CD_2Cl_2. These results unambiguously show the insertion of the CD_2 group into these two compounds.

In order to further study the reactivity of compound **47**, different alkyl halide reagents were used in attempts to perform oxidative addition across the rhodium metal center. Methyl iodide, benzyl chloride, 1,2-dichloroethane, 1,3-difluoropropane and 1,4-dichlorobutane were reacted with compound **47**. All reagents exhibited either multiple product formation or very low product yields. Attempts to isolate products were unsuccessful. The addition of diazomethane or (trimethylsilane)diazomethane to compound **47** at room temperature resulted no reaction.

2.4 Summary

In summary, a series of monomeric Group IX phosphinimine complexes **44-47** were readily prepared by a salt metathesis reaction under mild conditions. The observation that a solution of [RhCOD(*o*-$C_6H_4PPh_2NPh$)] **47** in methylene chloride slowly transformed into compounds **48** and **49** was unexpected. It was likely that complex **47** underwent oxidative addition of methylene chloride to the rhodium metal center, followed by the ligand rearrangement to yield the binuclear complexes. It should be noted that when steric bulk was introduced to the 2,6-position of the N-phenyl ring (compounds **44** and **45**), oxidative addition of CH_2Cl_2 on the rhodium center was inhibited.

Chapter Three
Synthesis of Group X Phosphinimine Complexes

3.1 Introduction

As described in the previous chapter, early transition metal catalyst systems continue to be a fruitful area of study; however, recently, much attention has been focused on late transition metal complexes. Brookhart,[8,9,23-25,185] Gibson[10-13] and Grubbs[14] have developed several late transition metal complexes which show high activities for the polymerization of simple olefins either in the presence or absence of co-catalyst. Our initial goal was to synthesize monomeric late metal phosphinimine complexes where steric bulk can be easily modified *via* typical synthetic routes for the phosphinimine ligand. Reactions involving Group X metals with phosphinimine ligands tended to form *bis*-ligand complexes. This chapter describes the synthesis of a series of Group X phosphinimine complexes.

3.2 Experimental

General Data: All preparations, ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, $^{7}Li\{^{1}H\}$ NMR and combustion analyses were performed under conditions similar to those described in Section 2.2. Ph_3PNPh was used as received from Aldrich Chemical Co. The ligand precursors $Ph_3PNSiMe_3$[125] and Ph_3PN^tBu[186] were prepared as described in literature.

Synthesis of [Ni(*o*-$C_6H_4PPh_2NPh)_2$] 67

A mixture of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$•Et_2O (0.13g, 0.16mmol) and $NiBr_2(PPh_3)_2$ (0.12g, 0.16mmol) was dissolved in THF (5 mL) at -20°C. The reddish solution was stirred overnight at RT, after which time the solvent was removed *in vacuo.* The residue was washed with pentane and recrystallized in benzene to afford red crystals. Yield: 0.17g (74%). ^{1}H NMR (300 MHz, C_6D_6) δ: 8.02 (d, 2H, $^3J_{H-H}$=8Hz, PC_6H_4), 7.65-7.59 (m, 8H, PPh_2), 7.05-6.92 (m, 18H), 6.89-6.83 (m, 2H, PC_6H_4), 6.77-6.71 (m, 2H, PC_6H_4), 6.68-6.66 (m, 6H, NPh, PC_6H_4). $^{13}C\{^1H\}$NMR (75.5 MHz, C_6D_6) δ: 170.4 (d, $^2J_{P-C}$=24Hz, PC_6H_4), 149.6 (s, PC_6H_4), 143.8 (s, PC_6H_5), 143.5 (s, PC_6H_4), 141.7 (s, PC_6H_5), 133.6 (d, $^2J_{P-C}$=10Hz, PPh_2), 132.7 (s), 131.5 (s, PC_6H_4), 131.3 (s), 130.4 (s, NPh), 121.8 (s, PC_6H_4), 120.1 (s, PC_6H_4). $^{31}P\{^1H\}$NMR (202.5 MHz, C_6D_6) δ: 33.7. Anal. Calc'd for $C_{48}H_{38}P_2N_2Ni$: C, 75.51; H, 5.02; N, 3.67. Found: C, 74.97; H, 5.27; N, 3.51.

Synthesis of [Ni(*o*-$C_6H_4PPh_2N(3,5\text{-}C_6H_3(CH_3)_2)$)$_2$] 68

A mixture of [Li(*o*-$C_6H_4PPh_2N(3,5\text{-}C_6H_3(CH_3)_2)$)$_2$]•$Et_2O$ (0.14g, 0.17mmol) and $NiBr_2(PPh_3)_2$ (0.13g, 0.17mmol) was dissolved in THF (5 mL) at RT. The reddish solution was stirred overnight, after which time the solvent was removed *in vacuo.* The residue was washed with pentane and recrystallized in benzene/THF to afford orange crystals. Yield: 0.08g (58%). ^{1}H NMR (500 MHz, C_6D_6) δ: 8.04 (d, 2H, $^3J_{H-H}$=8Hz, PC_6H_4), 7.74-7.62 (m, 8H, PPh_2), 7.08-6.95 (m, 14H), 6.92-6.83 (m, 2H, PC_6H_4), 6.81-6.73 (m, 2H, PC_6H_4), 6.64 (s, 4H, $NMe_2C_6H_3$), 6.26 (s, 2H, $NMe_2C_6H_3$), 1.90 (s, 12H, Me). $^{13}C\{^1H\}$NMR (75.5

MHz, C_6D_6) δ: 169.7 (d, $^2J_{P-C}$=25Hz, PC_6H_4), 149.5 (s, PC_6H_4), 144.3 (s, PPh_2), 142.8 (s, PC_6H_4), 141.7 (s, PPh_2), 135.6 (s, PPh_2), 133.3 (d, $^2J_{P-C}$ = 10Hz, PPh_2), 132.0 (s), 131.4 (s, PC_6H_4), 129.1 (s, $NMe_2C_6H_3$), 126.6 (d, $^2J_{P-C}$ = 14Hz, PC_6H_4), 122.4 (s), 121.7 (s, $NMe_2C_6H_3$), 20.9 (s, Me). $^{31}P\{^1H\}$NMR (202.5 MHz, C_6D_6) δ: 35.4. Anal. Calc'd for $C_{52}H_{46}P_2N_2Ni$: C, 76.21; H, 5.66; N, 3.42. Found: C, 74.80; H, 5.70; N, 3.14.

Synthesis of [Pd(*o*-$C_6H_4PPh_2NPh)_2$] 69

A mixture of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$•Et_2O (0.23g, 0.28mmol) and $PdCl_2$(COD) (0.08g, 0.28mmol) was dissolved in THF (5 mL) at RT. The mixture was stirred at RT for 6h during which time a fine grayish green solid precipitated from solution. The heterogeneous mixture was stirred overnight, after which time it was filtered through Celite. The yellow filtrate was concentrated to *ca.* 1 mL, and a yellow powder was precipitated after storage under benzene overnight. The yellow powder was filtered, dissolved in CH_2Cl_2 and recrystallized in the absence of light at -20°C. This compound decomposed in the presence of light. Yield: 0.12g (52%). ^1H NMR (500 MHz, C_6D_6) δ: 8.27 (d, 2H, $^3J_{H-H}$=8Hz, PC_6H_4), 7.72-7.67 (m, 8H, $^3J_{P-H}$=11Hz, $^3J_{H-H}$=7Hz, PPh_2), 7.25-7.22 (m, 2H, PC_6H_4), 7.02 (dt, 4H, $^3J_{H-H}$=7Hz, $^4J_{P-H}$=1Hz, NPh), 6.95 (dt, 8H, $^3J_{H-H}$=8Hz, $^4J_{P-H}$=2Hz, PPh_2), 6.81-6.79 (m, 8H), 6.73 (dd, 4H, $^3J_{H-H}$=8Hz, PPh_2), 6.62 (dd, 2H, $^3J_{H-H}$=7Hz, NPh). $^{13}C\{^1H\}$NMR (75.5 MHz, C_6D_6) δ: 171.2 (d, $^2J_{P-C}$=20Hz, PC_6H_4), 148.9 (s, PC_6H_4), 144.9 (s, PPh_2), 143.0 (s, PPh_2), 140.9 (s), 133.8 (d, $^2J_{P-C}$=10Hz, PPh_2), 131.6 (s), 131.1 (s), 130.0 (s), 129.9 (s, NPh), 127.2 (s, NPh), 125.9 (d, $^2J_{P-C}$=12Hz, PC_6H_4), 121.9 (s), 121.8 (s, PC_6H_4), 119.1 (s, PC_6H_4).

$^{31}P\{^{1}H\}$NMR (202.5 MHz, C_6D_6) δ: 27.8. Anal. Calc'd for $C_{48}H_{38}P_2N_2Pd$: C, 71.07; H, 4.72; N, 3.45. Found: C, 72.84; H, 5.36; N, 3.08.

Synthesis of [Pd(*o*-$C_6H_4PPh_2NPh$)(μ-Cl)]$_2$ 70

A mixture of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$•Et_2O (0.23g, 0.28mmol) and $PdCl_2$(COD) (0.08g, 0.28mmol) was dissolved in THF (5 mL) at RT. The mixture was stirred at RT for 6h during which time a fine grayish green solid precipitated from solution. The heterogeneous mixture was stirred overnight, after which time it was filtered through Celite and was subsequently dried *in vacuo.* The yellow residue was dissolved in CH_2Cl_2 and recrystallized at RT to afford tiny orange crystals. Yield: 0.04g (14%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 7.83-7.79 (m, 8H, PPh_2), 7.61-7.59 (m, 6H, PPh_2), 7.50 (m, 2H, PC_6H_4), 7.49-7.47 (m, 8H), 7.27 (dd, 2H, $^{3}J_{H-H}$=8Hz, PC_6H_4), 7.07-6.99 (m, 4H, NPh), 6.93-6.91 (m, 4H, NPh), 6.86 (d, 2H, $^{3}J_{H-H}$=7Hz, PC_6H_4), 6.82-6.79 (m, 2H, NPh). $^{13}C\{^{1}H\}$NMR (75.5 MHz, CD_2Cl_2) δ: 149.2 (d, $^{2}J_{P-C}$=18Hz, PC_6H_4), 147.1 (s, PC_6H_4), 142.2 (s, PPh_2), 135.4 (s, PPh_2), 133.2 (d, $^{2}J_{P-C}$=10Hz, PPh_2), 133.0 (s, PPh_2), 129.9 (s, NPh), 127.9 (s, NPh), 127.5 (s, PC_6H_4), 126.9 (s, NPh), 126.3 (d, $^{2}J_{P-C}$=11Hz, PC_6H_4), 125.2 (s, NPh), 124.3 (s, PC_6H_4), 121.5 (s, PC_6H_4). $^{31}P\{^{1}H\}$NMR (202.5 MHz, CD_2Cl_2) δ: 45.5. Anal. Calc'd for: C, 58.32; H, 3.87; N, 2.83. Found: C, 57.12; H, 3.85; N, 2.64.

X-Ray Structure Determinations of 67, 68, 69, 70

Data were collected at room temperature. No crystal decay was observed for any of the compounds. The resulting crystallographic values are given in Table 3.1. ORTEP drawings of **67**, **68**, **69, 70** are shown in Figures 3.5 - 3.8 respectively, with 30% thermal ellipsoids. Selected bond distances and angles are listed in the captions for Figure 3.5 - 3.8 respectively.

Table 3.1: Crystallographic Parameters for 67·1.5C_6D_6, 68·1.5C_6D_6, 69·CH_2Cl_2, and 70

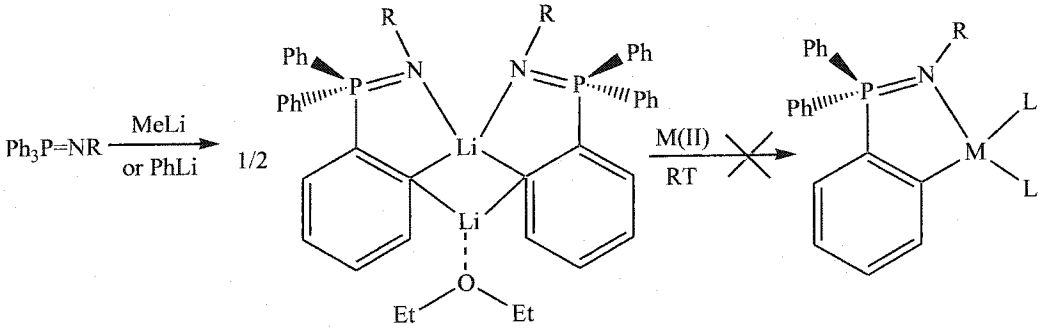
	67 · 1.5C_6D_6	**68** · 1.5C_6D_6	**69** · CH_2Cl_2	**70**
Formula	$C_{57}H_{47}N_2NiP_2$	$C_{83}H_{71}BrN\ P_4$ 1.5Ni	$C_{49}H_{40}Cl_2N_2P_2Pd$	$C_{24}H_{19}ClNPPd$
Formula weight	880.62	1374.26	896.07	494.22
a (Å)	11.703(7)	15.719(10)	14.543(9)	12.509(8)
b (Å)	13.353(8)	13.700(8)	10.026(6)	14.847(9)
c (Å)	17.039(10)	35.49(2)	29.194(17)	22.963(13)
α (°)	108.071(12)	90	90	90
β (°)	92.150(14)	90.364(12)	95.731(11)	99.363(12)
γ (°)	108.907(11)	90	90	90
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	P2/c	$P2_1/c$	C2/c
Volume ($Å^3$)	2366(2)	7643(8)	4235(4)	4208(4)
D_{calc} (gcm^{-1})	1.236	1.194	1.405	1.560
Z	2	4	4	8
Abs coeff,μ, mm^{-1}	0.517	1.021	0.677	1.094
Temp (K)	293(2)	293(2)	293(2)	293(2)
F(000)	922	2852	1832	1984
θ range (°)	1.75 - 23.27	1.30 - 23.22	1.40 - 23.23	2.15 - 23.23
Refl collected	10269	31881	17289	8873
R_{int}	0.0703	0.0613	0.0457	0.0209
Data $F_o^2>3\sigma(F_o^2)$	6705	10886	6031	3008
Parameters	559	816	505	253
R^a (%)	0.0540	0.0548	0.0337	0.0193
$R_w{}^a$ (%)	0.0557	0.1731	0.0689	0.0367
Peak, hole($e^-Å^{-3}$)	0.244, -0.238	1.25, -0.512	0.457, -0.491	0.214, -0.300
Goodness of fit	0.918	1.021	1.012	1.056

$$^aR = \sum ||F_o| - |F_c|| / \sum |F_o|,\ R_w = [\sum(|F_o| - |F_c|)^2| / \sum |F_o|^2]^{0.5}$$

3.3 Results and Discussion

The initial goal of this project was to synthesize neutral monomeric late metal phosphinimine complexes. Early attempts using triphenylphosphinimine, Ph_3PNR (R= ^tBu or $SiMe_3$) as ligand precursors were later proven to be unsuitable for the preparation of Group X late transition metal complexes. However, the less bulky triphenylphosphinimine ligand, Ph_3PNPh, permitted Group X phosphinimine complexes to be successfully synthesized, and these complexes will be discussed herein.

Two alternative routes were examined in efforts to synthesize Group X late metal phosphinimine complexes. In the first approach, a transmetallation reaction was used. The intermediate organolithium complexes **61** or **62** were synthesized according to literature procedures,[159] where lithiation was performed using methyl lithium at room temperature (for R= $SiMe_3$), or -78°C (for R= ^tBu). These organolithium complexes were then reacted with various Ni(II), Pd(II) or Pt(II) starting materials (Figure 3.1).



R = $SiMe_3$ **58**, ^tBu **59**, Ph **60** R = $SiMe_3$ **61**, ^tBu **62**, Ph **43** M = Ni(II), Pd(II), Pt(II)

Figure 3.1 Attempt to synthesize neutral late metal phosphinimine complexes using the transmetallation reaction.

Unfortunately, regardless of solvent or reaction conditions, the late metal precursor did not appear to coordinate to the triphenylphosphinimine ligand with R = ^{t}Bu or SiMe$_3$. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectroscopy demonstrated that multiple products were formed, most of which could not be identified, with the exception of the neutral ligand. In only one case, X-ray quality crystals were obtained from the product mixture. While reacting [Li(*o*-$C_6H_4PPh_2N^{t}Bu$)]$_2$•Et_2O **62** with $PdCl_2$ and $AgBF_4$ at elevated temperatures, colorless crystals were obtained. An X-ray diffraction study showed the compound to be [$Ph_3PNH^{t}Bu$][BF_4] and indicated that metathesis did not occur.

Since this strategy had failed to yield *ortho*-metallated phosphinimine complexes, another synthetic route was employed. In this second approach, *ortho*-bromination reaction was performed, where the organolithium intermediate was treated with bromine to yield *ortho*-brominated product. This intermediate was then reacted with zero valent Group X late metal complexes (such as Ni(COD)$_2$ or Pd(PPh_3)$_4$), in attempt to effect oxidative addition across the C_{aryl}-Br bond (Figure 3.2).

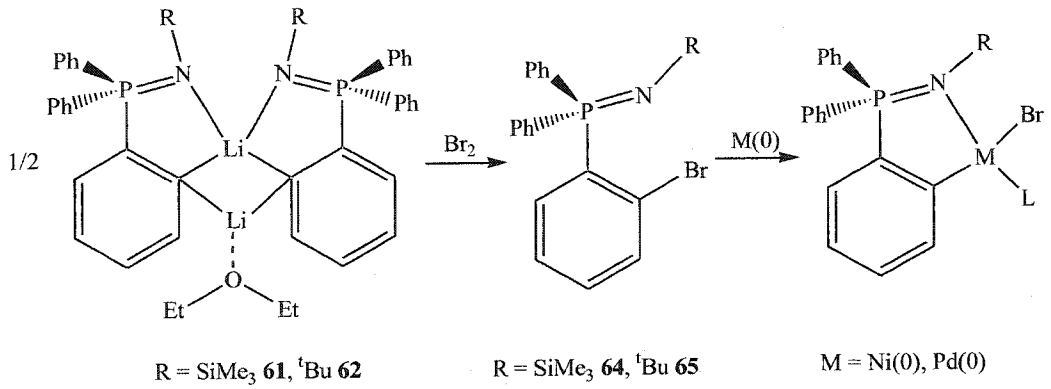


Figure 3.2 Attempt to synthesize late metal phosphinimine complexes using an *ortho*-brominated intermediate

However, problems occurred while performing the *ortho*-bromination reaction. Multiple products were formed from this step, and attempts to isolate the desired products were unsuccessful. After reacting with late transition metal starting materials, multiple unidentifiable products were formed. Changing the reaction conditions did not reduce the number of products. Attempts to purify product mixtures were unsuccessful. We propose that the steric demands of the ligand precluded the complex formation, thus a less bulky phosphinimine ligand, Ph_3PNPh, was used instead. The organolithium intermediate $[Li(o\text{-}C_6H_4PPh_2NPh)]_2 \bullet Et_2O$ was synthesized *in situ* as described in Chapter 2, and was then further reacted with Group X metal complexes. A red coloured Ni(II) organometallic compound $[Ni(o\text{-}C_6H_4PPh_2NPh)_2]$ **67** was obtained by reacting **63** with one equivalent of *bis*-triphenylphosphine nickel(II) bromide (Figure 3.3). It is noteworthy that attempts to synthesize monomer nickel(II) phosphinimine complexes using two equivalents of $NiBr_2(PPh_3)_2$ were also unsuccessful; unidentified green coloured paramagnetic products were formed.

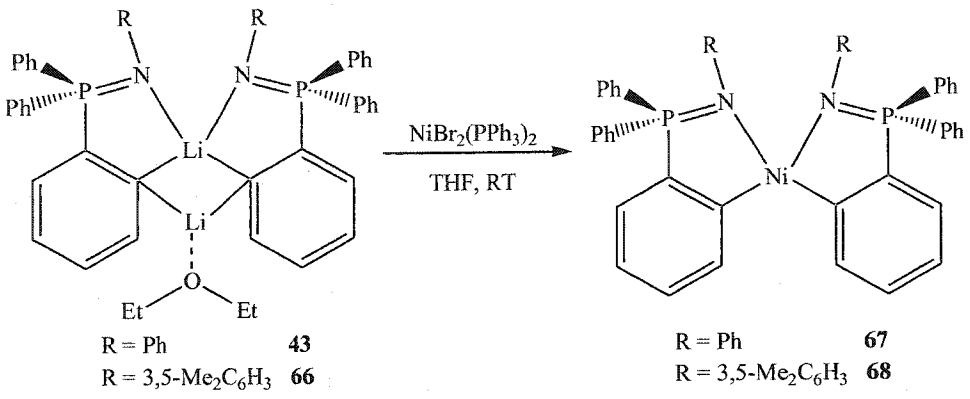


Figure 3.3 Synthesis of Ni(II) phosphinimine complexes

The isostructural yellow coloured organometallic Pd(II) complex [Pd(*o*-$C_6H_4PPh_2NPh$)]$_2$ **69** was synthesized by reacting the organolithium intermediate ***63*** with dichloro(1,5-cyclooctadiene)palladium(II) complex (Figure 3.4). In this particular reaction, in addition to the formation of compound **69**, an orange coloured Pd(II) chloro-bridged dimer **70** was also formed in low yield. Attempts to increase the yields of compound **70** by changing reaction conditions were unsuccessful. Decomposition of compound **69** in solution occurred gradually by precipitation of a black solid from the solvent after prolonged storage under light. The chloro-bridged compound **70** remained stable after prolonged storage under light.

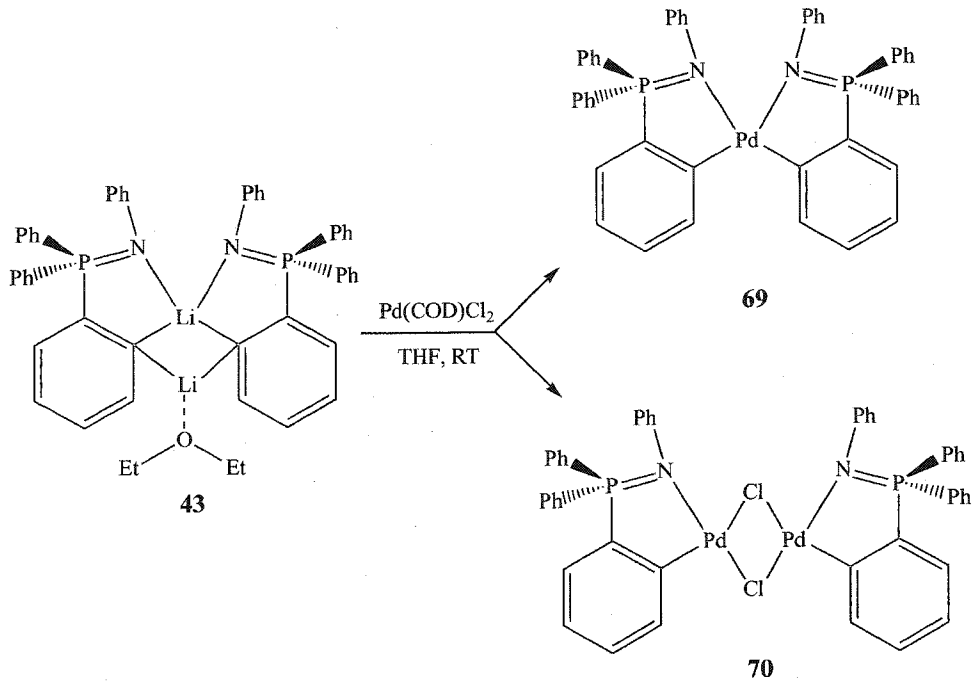


Figure 3.4 Reaction of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$•Et_2O **43** with $Pd(COD)Cl_2$

Compounds **67**, **69** and **70** were characterized spectroscopically by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR, as well as by elemental analysis and X-ray crystallography. ORTEP drawings of **67**, **69** and **70** are shown in Figures 3.5, 3.6 and 3.7 respectively. Structure of compound **67** and compound **69** were found to be isostructural. Both compounds **67** and compound **69** exhibit two M-C σ-bonds and two M←N donor bonds, giving a four-coordinate metal center with slightly distorted square planar geometry. The structure of [Ni(*o*-$C_6H_4PPh_2NPh)_2$] **67** displays two Ni-C σ-bonds with distances of 1.922(5) and 1.910(5) Å, respectively, which fall within the normal range of other Ni-C_{aryl} bonds such as 1.894(3) Å in [NiBr{*o*-$C_6H_4B(pin)$}$(PPh_3)_2$],[187] 1.8850(16) Å in [NiCl(C_6H_2{CH_2NMe_2}$_2$-2,6-$SiMe_3$-4)],[188] and 1.90(2) Å in *trans*-$(Me_3P)BrNi(\eta^2$-C(N^tBu)CH_2-*o*-C_6H_4)$NiBr(PMe_3)_2$.[189] The structure of [Pd(*o*-

$C_6H_4PPh_2NPh)_2]$ **69** also displays two Pd-C σ-bonds with distances of 2.002(4) and 2.011(4) Å, respectively. These are also typical for other Pd-C_{aryl} bonds, such as, 2.016(5) Å in $[Pd(C_6H_5)Br(PMe_3)CPh(NEt_2)]$,[190] 2.026(5) Å in $[PdBr\{o\text{-}C_6H_4B(pin)\}(PCy_3)_2]$,[187] and 2.000(3) Å in *trans*-$[PdCl\{C_6H_3(CO_2H)_2\text{-}2,5\}(PPh_3)_2]$.[191] The average N-$C_{aryl}$ bond lengths of compound **67** (1.431(6) Å) are slightly longer than average N-C_{aryl} bond lengths in compound **69** (1.412(4) Å). The P=N bond lengths of compound **67** (average of 1.616(4) Å), are also slightly longer than the P=N bond lengths of compound **69** (average of 1.604(3) Å), as well as the P=N bond distance of the parent phosphinimine Ph_3P=NPh (1.602(3) Å).[182] In both compounds **67** and **69**, the N-phenyl ring was twisted almost perpendicular away of the metallocyclic ring. The N(1)-Ni(1)-N(2) angle of 93.29(18)° for compound **67** which is slightly more acute then the corresponding N(1)-Pd(1)-N(2) angle of 94.87(11)° for compound **69**.

As described, compound **70** was also crystallized from the same reaction mixture as compound **69** in 14% yield. X-ray crystal structure determination revealed the structure of **70** to be dimeric, with the chloride atoms acting as bridging ligands (Figure 3.7). Each palladium atom in the metallacycle is in a slightly distorted square planar coordination environment. Interatomic distances from palladium to carbon, nitrogen and both the chlorine atoms are comparable to those found for similar complexes (Table 3.2). Compound **70** was the desired complex, where the bridging ligands can be split easily using tertiary phosphines forming monomeric derivatives. Unfortunately, attempts to increase the yield of compound **70** using varied reaction conditions were unsuccessful.

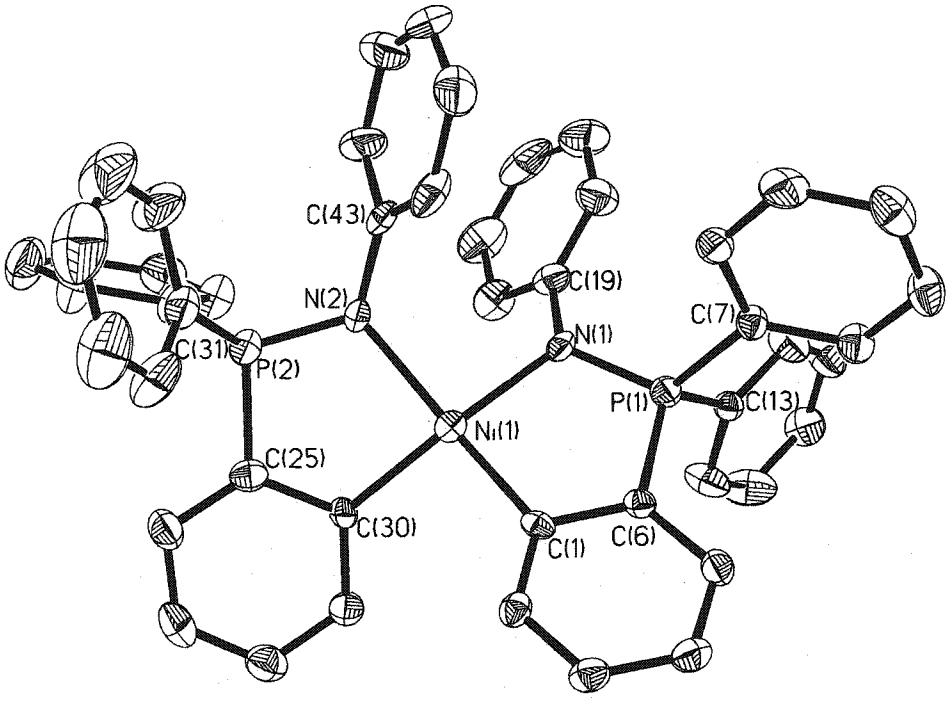


Figure 3.5 ORTEP drawing of **67**, 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized benzene molecule have been omitted for clarity. Selected bond distances and angles : Ni(1)-N(1) 1.997(4) Å, Ni(1)-C(1) 1.922(5) Å, P(1)-N(1) 1.619(4) Å; N(2)-Ni(1)-N(1) 93.29(18)°, N(1)-Ni(1)-C(1) 90.5(2)°, N(1)-P(1)-C(6) 103.3(3)°, P(1)-N(1)-Ni(1) 114.1(2)°, C(19)-N(1)-Ni(1) 122.8(4)°.

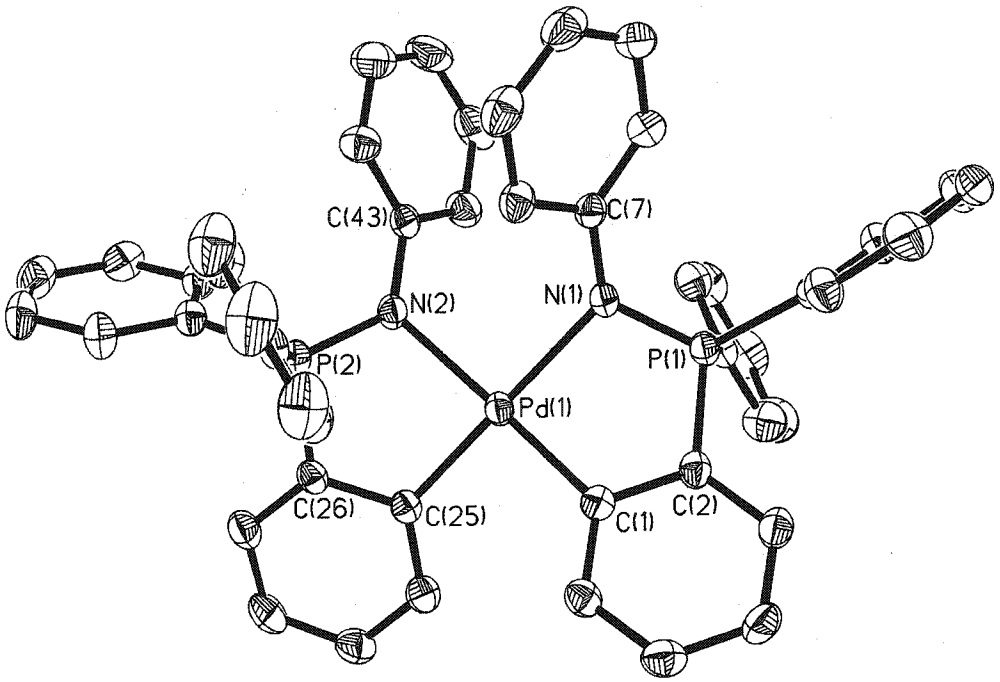


Figure 3.6 ORTEP drawing of **69**; 30% thermal ellipsoids are shown, hydrogen atoms and the co-crystallized methylene chloride molecule have been omitted for clarity. Selected bond distances and angles : Pd(1)-C(25) 2.002(4) Å, Pd(1)-N(2) 2.172(3) Å, N(2)-P(2) 1.607(3) Å, P(2)-C(26) 1.786(4) Å , N(2)-C(43) 1.405(5) Å; C(25)-Pd(1)-C(1) 94.36(15)°, C(25)-Pd(1)-N(2) 84.72(13)°, Pd(1)-N(2)-P(2) 102.74(15)°, N(2)-P(2)-C(26) 101.72(16)°, Pd(1)-N(2)-C(43) 127.5(2)°.

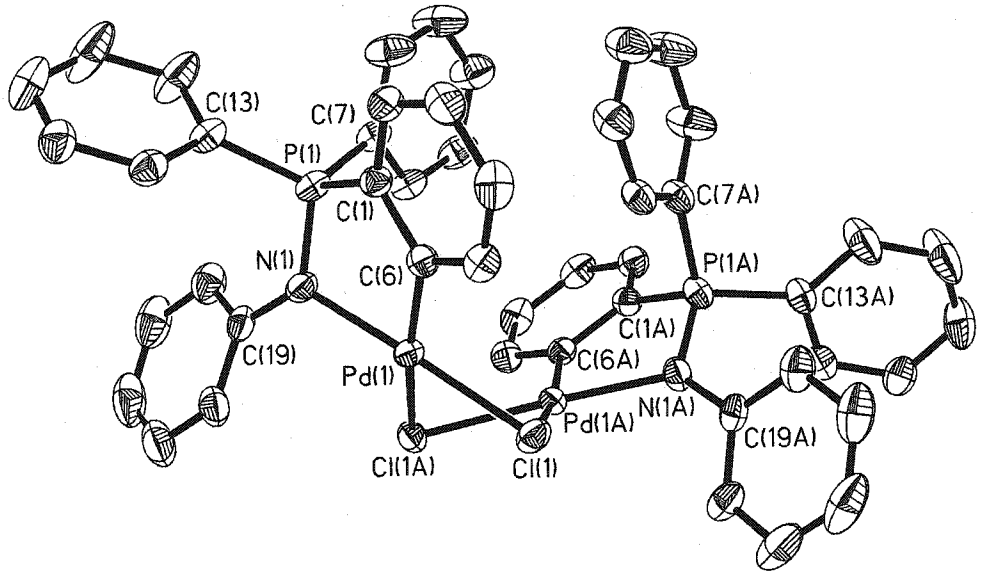


Figure 3.7 ORTEP drawing of **70,** 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances and angles : Pd(1)-Cl(1) 2.3502(12) Å, Pd(1)-Cl(1A) 2.5130(13) Å, Pd(1)-N(1) 2.047(2) Å, N(1)-P(1) 1.614(2) Å, P(1)-C(1) 1.784(3) Å, Pd(1)-C(6) 1.992(2) Å; Cl(1)-Pd(1)-Cl(1)#1 84.81(4)°, Cl(1)-Pd(1)-C(6) 96.09(8)°, C(6)-Pd(1)-N(1) 85.45(10)°, Pd(1)-N(1)-C(19) 122.32(16)°, Pd(1)-N(1)-P(1) 110.84(11)°, Pd(1)-C(6)-C(1) 116.50(18)°.

	Selected interatomic distances (Å)			
	Pd-N	Pd-C	Pd-Cl(1) (*trans* to Pd-N)	Pd-Cl(#1) (*trans* to Pd-C)
Compound **70**	2.047(2)	1.992(2)	2.3502(12)	2.5130(13)
[$CH_2Si(Me)_2C_6H_3(CH_2NMe_2)$-4-(PdCl)-3]$_2$ [192]	2.072(5)	1.977(5)	2.3105(14)	2.4732(15)
[Pd{(η^5-$C_5H_3CMeNCH_2CH(CH_2)_2CH_2$)Fe({($\eta^5$-$C_5H_5$)}($\mu$-Cl)]$_2$ [193]	2.058(2)	1.916(4)	2.339(1)	2.475(1)
(S,S)-Di-μ-chlorobis-{2-[2-(4-^{t}butyl) oxazolinyl]Ph-C,N} dipalladium (II)[194]	2.033(16)	1.997(8)	2.323(2)	2.455(2)

Table 3.2 Comparison of selected bond distances (Å) of compound **70** with similar complexes.

It was noteworthy that the bond distances between the palladium metal center and the two bridging chlorines are different. This phenomenon can be explained by using the *trans* influence of the N-donor atom *vs* the C_{aryl} atom. The stronger Pd-C_{aryl} bond causes a weakening of the Pd-Cl bond *trans* to the Pd-C_{aryl} σ-bond, relative to the Pd-Cl bond *trans* to the Pd←N bond.

Due to the success of coordinating nickel and palladium to the triphenylphosphinimine ligand (Ph_3PNPh), [$PtCl_2(COD)$] was also reacted with [$Li(o\text{-}C_6H_4PPh_2NPh)]_2 \cdot Et_2O$ **63** in an attempt to synthesize a Pt(II) analogue. The organolithium intermediate **63** was synthesized *in situ* as described in Chapter 2, and was reacted with [$PtCl_2(COD)$] in THF at room temperature. The $^{31}P\{^1H\}$ spectrum showed two sets of signals with platinum coupling satellites, centered at 36.6 ppm ($^2J_{Pt\text{-}P}$ = 126Hz), as well as 33.9 ppm ($^2J_{Pt\text{-}P}$ = 138 Hz) which indicated the presence of platinum in the complexes. $^{13}C\{^1H\}$NMR

spectroscopy showed a downfield C-Pt resonance centered at 167.4 ppm, confirming the presence of the C-Pt bond. Due to the similar solubility of the two complexes, attempts to separate them were unsuccessful. In this case, neither single crystals suitable for X-ray analysis nor a reliable elemental analysis determination could be received, very limited information could be obtained from the spectroscopic data. Though based on the similar types of *bis*-ligand complexes **67** and **69** were formed from the reaction of $[Li(o\text{-}C_6H_4PPh_2NPh)]_2 \cdot Et_2O$ with $NiBr_2(PPh_3)_2$ and $PdCl_2(COD)$ respectively, complex with the structure of $[Pt(o\text{-}C_6H_4PPh_2NPh)_2]$ was proposed as one of the possible products. Further investigations are necessary to confirm the exact structure of the products.

A similar synthetic approach has also been applied to the (3,5-dimethylphenylimino)triphenylphosphine ligand system, $Ph_3P{=}N(3,5\text{-}C_6H_3(CH_3)_2)$ **26**, to give the *bis*-ligand nickel (II) complex **68**. Compound **26** was lithiated using Li^nBu *in situ* as described in previous chapter, and was then reacted with $NiBr_2(PPh_3)_2$ in THF at room temperature. Orange X-ray quality crystals were obtained and the X-ray determination study indicated that the metal complex had a structure shown in Figure 3.9. The nickel center has a slightly distorted square planar geometry, and has similar structure with compound **67**. The $^{31}P\{^1H\}$ NMR spectrum shown a signal centered at 35.4 ppm, and ^1H and $^{13}C\{^1H\}$ NMR data confirmed the formation of the complex. An ORTEP drawing of compound **68** is shown in Figure 3.8.

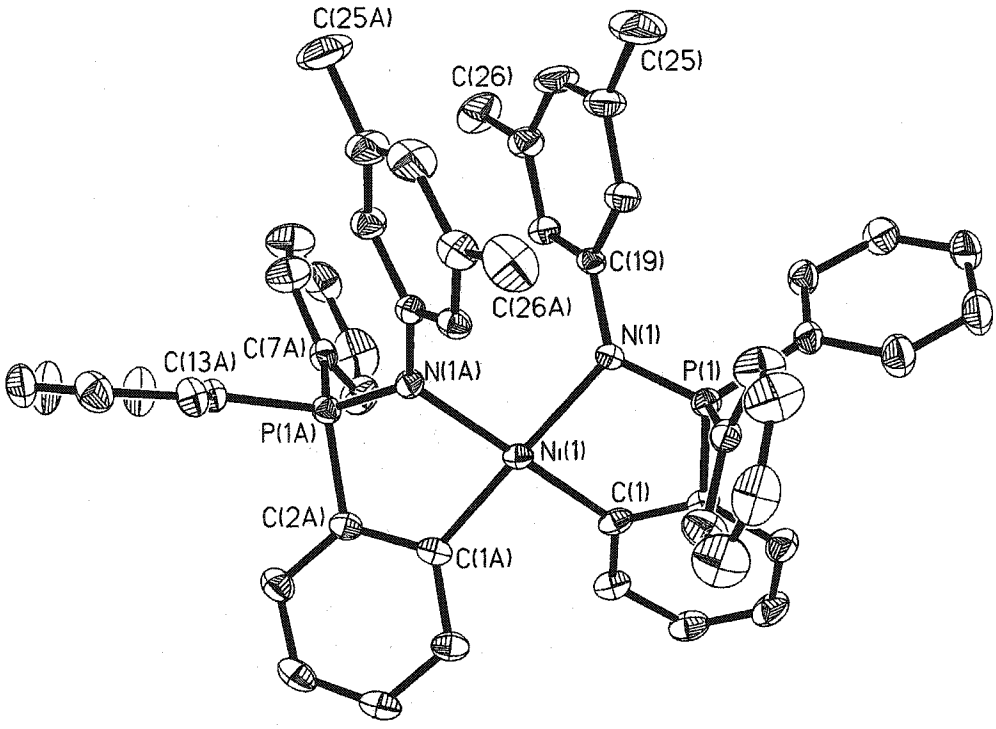


Figure 3.8 ORTEP drawing of **68**, 30% thermal ellipsoids are shown, hydrogen atoms, the co-crystallized benzene and $NiBr(PPh_3)_3$ molecule and have been omitted for clarity. Selected bond distances and angles: Ni(1)-N(1) 2.016(6) Å, Ni(1)-C(1) 1.907(8) Å, P(1)-N(1) 1.606(6) Å; N(1A)-Ni(1)-N(1) 94.8(3)°, N(1)-Ni(1)-C(1) 85.9(3)°, P(1)-N(1)-Ni(1) 108.5(3)°, C(19)-N(1)-Ni(1) 125.4(5)°.

Noteworthy in the transmetallation reaction of [Li(*o*-$C_6H_4PPh_2NPh$)]$_2$•Et_2O **63** and [Li(*o*-$C_6H_4PPh_2N$(3,5-$C_6H_3(CH_3)_2$))]$_2$•Et_2O **66** with $NiBr_2(PPh_3)_2$, a side product, $NiBr(PPh_3)_3$ was obtained. X-ray crystallography unambiguously showed the formation of the Ni(I) compound. Similar redox chemistry was observed by Stalke *et al.*[161] in the reaction of [Li(*o*-$C_6H_4PPh_2NSiMe_3$)]$_2$•Et_2O with $CuCl_2$, which generated a reductive coupling product [(*o*-$C_6H_4PPh_2NSiMe_3)_2$] and an organocopper (I) compound. Though in our case, the ligand coupling product was not isolated, we propose that a similar compound with the structure [(*o*-$C_6H_4PPh_2NR)_2$] (R = Ph, or 3,5-$C_6H_3(CH_3)_2$) is a likely side product in the transmetallation of compound **63** and compound **66** with $NiBr_2(PPh_3)_2$.

3.4 Summary

In summary, attempts to coordinate the *ortho*-lithiated compound [Li(*o*-$C_6H_4PPh_2NSiMe_3$)]$_2$•Et_2O **61** or [Li(*o*-$C_6H_4PPh_2N^tBu$)]$_2$•Et_2O **62** to Group X late transition metals using various approaches were unsuccessful. Conversely, transmetallation of the *ortho*-lithiated triphenylphosphinimine ligand, [Li(*o*-$C_6H_4PPh_2NR$)]$_2$•Et_2O (R = Ph **43** or (3,5-$C_6H_3(CH_3)_2$) **66**) results in a side arm N-donating chelating organometallic ligand. In all the metal complexes mentioned, the triphenylphosphinimine ligand moiety acts as a side-arm donating group, donating electron density to the metal center through the imine nitrogen atom. The reaction of **43** or **66** with $NiBr_2(PPh_3)_2$ and $PdCl_2$(COD) results in the formation of compounds [Ni(*o*-$C_6H_4PPh_2NPh)_2$] **67**, [Ni(*o*-$C_6H_4PPh_2N$(3,5-$C_6H_3(CH_3)_2$))$_2$] **68**, and [Pd(*o*-$C_6H_4PPh_2NPh)_2$] **69** as major

products. The chloro-bridged dimer, [Pd(*o*-$C_6H_4PPh_2NPh$)(μ-Cl)]$_2$ **70** was also isolated as a minor product when $PdCl_2$(COD) was used as a metal precursor.

Chapter Four

Summary

The research herein has described synthetic chemistry of Group IX and Group X phosphinimine complexes. The results provide insight into the coordination chemistry of Group IX and Group X late transition metal with phosphinimine ligands.

A series of Group IX phosphinimine complexes were synthesized *via* salt metathesis reactions under mild conditions. The oxidative addition of dichloromethane, followed by ligand rearrangement was observed in compounds **46**, **47**, **52**, as well as the analogous iridium compound **53**. A possible mechanism for this reaction could involve the initial formation of the chloromethyl (Cl-CH_2-M-Cl) derivative, and then undergo reductive elimination to form a C-C bond. The compound will then undergo oxidative addition again to form the products. This process reacted rapidly, therefore intermediate was not observed by spectroscopic methods. It was found that the inclusion of bulky aryl substituents on the imine nitrogen inhibited the oxidative addition reaction. Steric congestion appears to be an important factor in influencing the facile addition reaction. Future research involving these complexes will be focused on the study of ligand effects upon a variety of processes that are, catalyzed by Group IX metal complexes, such as hydroformylation.

Additionally, a series of Group X phosphinimine complexes have been prepared. The first synthetic goal of this project was the preparation of monomeric Group X transition metal phosphinimine complexes. Though, we demonstrated that reacting Group X metals with phosphinimine ligands tended

to form *bis*-ligand complexes. These compounds are anticipated not to act as practical polymerization catalysts. However, in one case where $PdCl_2$(COD) was used as the metal precursor, the desired complex was formed in very low yield. Further attempts to increase the yield of compound **69** by optimizing the reaction condition is worth pursuing.

In conclusion, the research described and discussed in this thesis has established the coordination chemistry of both Group IX and Group X complexes containing phosphinimine ligands. The study of steric influences toward oxidative addition of dichloromethane in group IX phosphinimine complexes was also performed. These synthetic fundamental accomplishments described herein lay the foundation for investigation into potential catalytic reactions.

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